MIKROCHEMIE

VEREINIGT MIT

MIKROCHIMICA ACTA

BEIRAT:

H. K. BARRENSCHEEN-WIEN · W. BÖTTGER-HANNOVER
H. V. A. BRISCOE-LONDON · F. EMICH-GRAZ · B. FLASCHENTRÄGER-ZÜRICH · A. FRANKE-WIEN · M. FURTER-ZÜRICH · E. GLEDITSCH-OSLO · J. HEYROVSKÝ-PRAG · O. HÖNIGSCHMID-MÜNCHEN · H. LIEB-GRAZ · J. LINDNER-INNSBRUCK · C. J. VAN NIEUWENBURG-DELFT
E. SPÄTH-WIEN · P. A. THIESSEN-BERLIN · P. WENGER-GENF
L. ZECHMEISTER-PÉCS

SCHRIFTLEITUNG:

A. A. BENEDETTI-PICHLER
NEW YORK

W. F. EHRET
NEW YORK

J. W. MATTHEWS
LONDON

F. HECHT
WIEN

BAND XXVII, VIERTES HEFT
MIT 148 TEXTABBILDUNGEN
(ABGESCHLOSSEN AM 9. SEPTEMBER 1939)

WIEN
VERLAG VON JULIUS SPRINGER
1939

Mikrochemie

Die Zeitschrift

„Mikrochemie vereinigt mit Mikrochimica Acta"

erscheint zwanglos in Heften, die in kurzer Folge zur Ausgabe gelangen. Je 3—4 Hefte bilden einen Band. Der Preis des Bandes beträgt RM 40.—.

In der Regel können Originalarbeiten nur Aufnahme finden, wenn sie nicht mehr als einen Druckbogen umfassen. Sie werden mit dem Datum des Eingangs versehen und der Reihe nach veröffentlicht, sofern die Verfasser die Korrekturen rechtzeitig erledigen. Abhandlungen polemischen Inhaltes werden nur dann zugelassen, wenn sie tatsächliche Richtigstellungen enthalten. Die Entscheidung über die Aufnahme steht allein der Schriftleitung zu.

Manuskripte sind zu senden an die

Schriftleitung der „Mikrochemie vereinigt mit Mikrochimica Acta"
Wien I, Schottengasse 4;

aus den Vereinigten Staaten von Nordamerika an

Editors of Mikrochemie, Chemistry Department, New York University, Washington Square, New York, N. Y./USA.

Beiträge werden in deutscher, englischer, französischer oder italienischer Sprache angenommen. Es wird ausdrücklich darauf aufmerksam gemacht, daß mit der Annahme des Manuskriptes und seiner Veröffentlichung durch den Verlag das ausschließliche Verlagsrecht für alle Sprachen und Länder an den Verlag übergeht, und zwar bis zum 31. Dezember desjenigen Jahres, das auf das Jahr des Erscheinens folgt. Es können somit grundsätzlich nur Arbeiten aufgenommen werden, die vorher weder im Inlande noch im Auslande veröffentlicht worden sind und die auch nachträglich nicht anderweitig zu veröffentlichen sich der Verfasser verpflichtet.

Die Verfasser erhalten eine *Fahnenkorrektur*; Revisionen können grundsätzlich nicht geliefert werden. Bei Beiträgen von in weit entfernten oder überseeischen Ländern wohnenden Mitarbeitern werden die Korrekturen dieser Beiträge im Interesse eines beschleunigten Erscheinens von der Schriftleitung gelesen. Wird jedoch die Übersendung von Fahnenabzügen zur Korrektur gewünscht, so muß die sich daraus ergebende spätere Veröffentlichung von dem Verfasser in Kauf genommen werden.

Die Verfasser erhalten für ihre Arbeit einen Unkostenersatz von RM 20.— für den Druckbogen, im Höchstfalle RM 30.— für eine Arbeit.

Die Mitarbeiter erhalten von Abhandlungen 75 Sonderdrucke unentgeltlich. Weitere 125 Exemplare werden, falls bei Rücksendung der Korrektur bestellt, gegen eine angemessene Entschädigung geliefert. Darüber hinaus gewünschte Exemplare müssen zum Bogennettopreise berechnet werden. Mit der Lieferung von Dissertationsexemplaren befaßt sich die Verlagsbuchhandlung grundsätzlich nicht; sie stellt jedoch den Doktoranden den Satz zwecks Anfertigung der Dissertationsexemplare durch die Druckerei zur Verfügung.

Im Interesse der unbedingt gebotenen Sparsamkeit wollen die Herren Verfasser auf knappste Fassung ihrer Arbeiten und Beschränkung des Abbildungsmaterials auf das unbedingt erforderliche Maß bedacht sein.

Verlag von Julius Springer in Wien I

XXVII. Band — Inhaltsverzeichnis — 4. Heft

Seite

Whitmore, W. F. and C. A. Wood. Chemical Microscopy of Some Toxicologically Important Alkaloids 249

Hynes, W. A. and L. K. Yanowski. Studies on the Application of Salts of Complex Cations to the Microscopic Detection of Anions. IX. Monoaquopentamminocobaltic Chloride (Roseocobaltic Chloride) 335

Benedetti-Pichler, A. A. and R. A. Paulson. Quantitative Microdeterminations with the Use of Analytical Balances 339

Buchbesprechungen 348

Autorenverzeichnis 351

Contribution from the Polytechnic Institute of Brooklyn

Chemical Microscopy of Some Toxicologically Important Alkaloids

By

W. F. Whitmore and **C. A. Wood***

(Received, November 16, 1937)

It is our belief that many of the available confirmatory tests for alkaloids are not sufficiently reliable. Color tests, so often recommended,[1] are easily obtained but nevertheless too often do not definitely establish the presence of the suspected substance. For example, the *Vitali* reaction for aconite alkaloids, which produces a purple coloration,[2] gives similar or confusing results with veratrin, pseudo aconitin and strychnine. As to the sublimation of alkaloids,[3] it has lately[4] been pointed out that the appearance of the sublimates under the microscope is only occasionally useful for purposes of identification. It is not surprising that the sublimation temperature has not been found generally useful, since it is too poorly defined. The determination of the melting points of the free bases or their derivatives in the capillary or still better under the microscope[5] offers an excellent means of identification. The degree of purity required for a satisfactory melting point determination may, however, often be very difficult to attain. A number of investigators[6,7,8,9,10] have described

* The work herein reported represents a portion of that presented by Mr. *Wood* as his dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

[1] *H. T. Clark*, Handbook of Organic Analysis, London 1928.

[2] *R. Witthaus* and *T. Becker*, Medical Jurisprudence and Toxicology, IV, New York 1911.

[3] *A.* and *M. Blyth*, Poisons, their Effects and Detection, London 1906.

[4] *L.* and *A. Kofler* and *A. Mayrhofer*, Mikroskopische Methoden in der Mikrochemie, Vienna and Leipzig 1936.

[5] *L. Kofler* and *F. A. Müller*, Mikrochemie **22**, 43 (1937).

[6] *Caille* and *E. Viel*, C. R. Acad. Sciences **176**, 1156 (1923).

[7] *V. Cordier*, Mh. Chem. **43**, 347 (1904).

[8] *W. Cumming* and *D. Brown*, J. Soc. Chem. Ind. **47**, 84 T (1928).

[9] *M. Wagenaar*, Pharmaz. Weekbl. **64**, 1085 (1927); Chem. Abstracts **22**, 136 (1928).

[10] *L. Rosenthaler*, Arch. Pharmac. u. Ber. dtsch. pharm. Ges. **256**, 319 (1927).

microchemical slide tests for the alkaloids, but much of this work has been of a somewhat haphazard nature, i. e., with one or two alkaloids or an isolated group of them, and it should be realized that a microchemical test for a given alkaloid is valueless if the reactions of the particular reagent with other alkaloids is unknown. *Stephenson*,[11] *Amelink*,[12] *Grutterink*,[13] *Rosenthaler* and *Gorner*[14] were particularly interested in the reactions of general alkaloid reagents with a series of the bases. Of course, a general reagent, by its very nature, introduces the possibility of interference of other alkaloids. If a number of alkaloids give precipitates with one reagent, there is considerable possibility that the crystalline phases formed will be rather similar. The optical properties, which are easily determined with the polarizing microscope, have in general been neglected by the investigators in this field. A few isolated descriptions have been given by *Grutterink*,[13] and *Amelink*[12] gives a number of these properties in connection with the crystallizations produced by his six reagents.

In the work reported in this paper, the degree of specificity of every test was determined by its application to all of the alkaloids to be considered. Specificity in a strict sense could not be established in any case, since this would require an extension of the investigation to include all known alkaloids. The scope of such an enterprise appeared entirely too large, but an attempt has been made to include at least those substances which are frequently met with in toxicological investigations, i. e.,

Local Anesthetics: beta eucaine, cocaine, procaine, stovaine;
Cinchona Alkaloids: cinchonine, cinchonidine, quinine, quinidine;
Opium Alkaloids: codeine, dionine, heroine, morphine, narcotine, papaverine;
Nux Vomica Alkaloids: brucine, strychnine;
Purine bases: caffeine, theobromine;
Miscellaneous: atropine, nicotine.

A few rare alkaloids have been included since they sometimes accompany the more common ones because of their occurrence in the same source, and because of the similarity in their chemical properties.

More than forty reagents were systematically applied to all of the listed bases, and the comparison of the results led to the discovery of confirmatory tests of satisfactory specificity. A complete record of the investigation is given on the following pages to provide the user of the article with the facts on which the recommendations of certain tests are

[11] *C. H. Stephenson*, Some Microchemical Tests for Alkaloids, London 1921.

[12] *F. Amelink*, Schema zur mikrochemischen Identifizierung von Alkaloiden, Amsterdam 1934.

[13] *Alide Grutterink*, Z. analyt. Chem. **51**, 175 (1910).

[14] *L. Rosenthaler* and *P. Gorner*, ibid. **49**, 340 (1910).

based. To facilitate the recognition of test forms and to impart to the tests a maximum of certainty, all those properties of crystalline precipitates were determined which can be rapidly ascertained with the use of the polarizing microscope. Birefringency was designated as weak or strong. The angle of extinction was determined, and the sign of elongation obtained with the selenite plate. The term positive elongation is used to indicate that the slower component of light vibrates approximately parallel to the longer direction of the crystal; conversely, negative elongation was used to denote vibration of the faster component approximately parallel to the outstanding direction of form. As another easily observable feature, pleochroism was reported; profile or silhouette angles[15] were occasionally measured. The determination of refractive indices was dismissed as too time consuming.

Selection and Preparation of Reagents

I. Halogen Reagents

1. *Br_2 in NaBr.* The solution was prepared in accordance with *Fulton*'s formula,[16] as follows:

NaBr.....	5 g.	
H_2O.....	90 ml.	
H_2SO_4 (1:3).....	10 „	Saturate with Br_2.

2. *ICl_3.* A solid crystal is added to the test drop. Since *Wagner*'s reagent (iodine in KI) is very useful,[11] it was thought ICl_3 derivatives might also prove characteristic.

II. Oxygen Acids and Salts Including Organic Salts

3. *(A) $HClO_4$.* A 5% aqueous solution was employed. *Chamot* and *Mason*[17] describe strychnine perchlorate as a test for the perchlorate ion.

(B) NH_4ClO_4. A 5% aqueous solution was employed. Some alkaloid perchlorates have been described by *V. Cordier*.[7]

4. *$Na_2B_4O_7$.* This salt was used in 5% solution in water. The reagent was investigated principally from the standpoint of effecting separations of the alkaloids.

5. *NH_4VO_3.* A 5% solution of the salt in water was employed in the hope of forming insoluble crystalline vanadates.

6. *Potassium anthraquinone sulfonate.* A crystal or two of the solid salt was added to the test drop and then warmed. This reagent was

---

[15] *A. C. Shead*, Ind. Eng. Chem., Anal. Ed. **9**, 496 (1937).

[16] *C. C. Fulton*, Amer. J. Pharmac. **104**, 244 (1932).

[17] *E. M. Chamot* and *C. W. Mason*, Handbook of Chemical Microscopy, I and II, New York 1932.

described by *Rosenthaler*,[18] and later used by *Amelink*[12] in connection with the Lobelia alkaloids.

7. *Potassium xanthate.* Potassium ethyl xanthate was originally used for characterization of metals.[17] It has been described as a test for some of the alkaloids.[19] The reagent was added to the test drop in solid form. When alkaloid xanthates were obtained, the reactions with other xanthate esters such as the isopropyl were investigated.

8. *Sodium veronalate.* The sodium salt of diethyl barbituric acid was employed in 5% aqueous solution.

9. *Cupferron.* This reagent was employed by adding a solid crystal (about 1 mg.) to the test drop and then stirring.

10. *Potassium acid phthalate.* This salt was used in 5% solution in water in the hope that test forms of acid phthalates of the alkaloids might be obtained suitable for identification purposes.

11. *KBr.* A 15% aqueous solution of this salt was used.

III. Salts Leading to Complex or Double Salt Formation

12. *(A) $SnCl_2$.* Six grams of $SnCl_2 \cdot 2H_2O$ were dissolved in 100 ml. of approx. 3 *N* HCl.

(B) $SnBr_2$. Tests were run with 5 to 10 mg. of NaBr added to a drop of the $SnCl_2$ reagent before addition to the alkaloid solution. For convenience, the reagent is designated as $SnBr_2$, which is the precipitating agent in this case.

13. *$TiCl_3$.* This reagent was employed in 15% aqueous solution. No records of alkaloid derivatives of this element were found in the literature, yet tin, in the same periodic group, offers some promise as an alkaloid reagent.[16]

14. *$BiCl_3$.* Seven grams of $Bi(NO_3)_3 \cdot 5\,H_2O$ were dissolved in 100 g. of approximately 3 *N* HCl.

15. *Potassium antimonyl tartrate.* A 5% solution of the reagent in water was employed, since alkali and a few other metals form complex tartrates of the formula $M(SbO)(C_4H_4O_6) \cdot H_2O$, it was hoped that alkaloid salts of similar character might form.

16. *$AsCl_3$.* A 5% solution of As_2O_3 in approximately 2 *N* HCl was employed. Because of the close chemical relationship, it was thought arsenic derivatives might be obtained similar to those with antimony.

17. *Mercurochrome.* Dibrom-oxy-mercuri-fluorescein was studied because of the wide applicability of the inorganic mercury salts in alkaloid precipitation. The ordinary 2% medicinal preparation was employed.

---

[18] *L. Rosenthaler*, Amer. J. Pharmac. **101**, 196 (1929).

[19] *E. Navarro*, Chem. Abstracts **20**, 2227 (1926).

IV. Anions of Complex Salts or Acids

18. *$NaAgI_2$*. This reagent is recommended by *Fulton*[16] for cocaine. His formula follows:

Five grams $AgNO_3$ and 75 g. NaI dissolved in 100 ml. water. In making tests, at least as much reagent as alkaloid solution is employed. The test drop is then mixed well so that any silver iodide precipitated by dilution will be redissolved.

19. *(A) $KAuI_2$*. Just sufficient KI was added to 1% $AuCl_3$ to redissolve the original precipitate.

(B) $HAuI_2$. The above reagent was used acidified with an equal volume of 0,5 *N* HCl. It was hoped that characteristic test forms would be obtained with the less basic alkaloids.

20. *(A) $NaAuBr_4$*. The reagent designated as $NaAuBr_4$ was prepared by addition of 5 g. of NaBr to 100 ml. of an aqueous solution containing 5 g. of $HAuCl_4 \cdot 3\ H_2O$.

(B) $HAuBr_4$.

$HAuCl_4 \cdot 3\ H_2O$	5 g.
5% HBr in H_2O	100 ml.

It was thought the gold bromide derivatives might be useful because of the wide application of $AuCl_3$ derivatives in alkaloid identification.

21. *$IrCl_4$*. Iridium tetrachloride was employed in 5% solution in water. The platinum group metals were investigated because of the wide use of platinum itself. *Whitmore* and *Schneider*[20] have employed certain alkaloids in the identification of these metals.

22. *$RhCl_3$*. Rhodium trichloride was used in 5% aqueous solution.

23. *$RuCl_3$*. Ruthenium trichloride was used in 5% aqueous solution.

24. *Na_2OsCl_6*. Sodium chlorosmate, 5% solution in water, was stabilized by bubbling chlorine gas through the solution until saturation was attained. A reagent was thus obtained yielding no apparent decomposition over a two year period.

25. *(A) H_2PtCl_6* in 20% *HBr*.

$H_2PtCl_6 \cdot 6\ H_2O$	6 g.
20% HBr in water	100 ml.

(B) H_2PtCl_6 in 5% *HBr*.

$H_2PtCl_6 \cdot 6\ H_2O$	6 g.
5% HBr in water	100 ml.

(C) Na_2PtBr_6. For convenience, the reagent is designated as shown.

$H_2PtCl_6 \cdot 6\ H_2O$	6 g.
NaBr.....	5 g.
H_2O.....	100 ml.

[20] *W. F. Whitmore* and *H. Schneider*, Mikrochemie **17**, 279 (1935).

Since chlorplatinic acid is one of the most useful of alkaloid reagents, it was thought advisable to study the effect of substituting the bromide ion in this reagent, especially with reference to the weakly basic alkaloids and with a view toward micro separations.

26. *K_2PtI_6*. To 1 ml. 6% $H_2PtCl_6 \cdot 6\ H_2O$, add 9 ml. 15% KI in H_2O. This reagent was expected to yield crystalline derivatives with those of the less basic alkaloids which showed only slight tendency to yield insoluble complex platinochloride salts. *Amelink*[12] reports some platinic iodide derivatives obtained by adding a little saturated sodium iodide solution to the platinic chloride reagent.

27. *Cs_2CdI_4*. This reagent was employed by *Rosenthaler*.[21] 1,8 g. CdI_2 and 5 g. of CsI are dissolved in H_2O and diluted to 100 ml. The reagent was studied with particular regard to the effect of the cesium iodide on precipitations as compared with results obtained with CdI_2. *Fulton*,[16] states that cadmium iodide gives results similar to *Marme*'s reagent (potassium cadmium iodide).

28. *(A) CdI_2*. A 5% solution of CdI_2 in water was employed.

(B) $CdBr_2$. A 5% solution of $CdBr_2$ in water was employed.

(C) $Cd(NO_3)_2 + NH_4SCN$. $Cd(NO_3)_2$, 5% solution in water. To a drop of this solution, a crystal of NH_4SCN (3 to 4 mg.) is added, the resulting reagent is connected to the alkaloid test drop with the aid of a stirring rod. This reagent, and the other metallo thiocyanate reagents, were employed in the hope of forming complex alkaloid thiocyanates suitable for test purposes.

(D) $CdCl_2$. A solution of 6% $CdCl_2 \cdot 2\ H_2O$ in water was employed.

29. *(A) K_2HgBr_4*.

$HgBr_2$	2 g.
KBr	1,32 g.
H_2O	100 ml.

(B) K_2HgBr_4, acidified. The above reagent was used in acid form by adding one drop of approximately 0,5 *N* HCl to the drop of reagent before addition to the alkaloid solution. *Rosenthaler*,[22] describes some alkaloid mercuric bromides.

30. *$K_2Hg(SCN)_4$*. The reagent employed was that of *Chamot* and *Mason*[17], Vol. 2. The preparation follows:

"Dissolve 3 to 5 parts of KSCN and 1 part of $Hg(SCN)_2$ in a minimum quantity of water and evaporate in a desiccator. Collect the first crop of tabular crystals, wash with alcohol and dry."

The salt was used in 5% solution in water.

---

[21] *L. Rosenthaler*, Der Nachweis organischer Verbindungen, Stuttgart 1926.
[22] *L. Rosenthaler*, Amer. J. Pharmac. **100**, 757 (1928).

31. *Potassium thallic iodide.* The reagent was prepared as follows:

$TlC_2H_3O_2$	5 g.
KI	75 g.
H_2O	100 ml.,

add I_2 crystals until the thallous salt dissolves.

32. *(A) H_2SnCl_6.* A 7% solution of $SnCl_4 \cdot 5\ H_2O$ in approx. 3 *N* HCl was employed. *Fulton*[23] reports a cocaine derivative with chlorstannic acid.

(B) $H_2SnCl_6 + KBr$. For increased sensitivity, the above reagent was employed after first adding a crystal (5 to 10 mg.) of KBr to the reagent drop before addition to the alkaloid solution.

33. *$HSbCl_4$.* A 5% solution of $SbCl_3$ in 6 *N* HCl was employed.

34. *$MnSO_4 + NH_4SCN$.* $MnSO_4 \cdot 4\ H_2O$ was employed in 7% solution in water. A crystal of NH_4SCN was added to a drop of this solution before addition to the alkaloid test drop. It was hoped that complex alkaloid manganese thiocyanates might develop.

35. *$Co(NO_3)_2 + NH_4SCN$.* $Co(NO_3)_2 \cdot 6\ H_2O$ was employed in 7% solution in water. A crystal of NH_4SCN was added to a drop of this solution before addition to the alkaloid test drop in the hope of developing complex alkaloid cobalt thiocyanates.

36. *$Cr_2(SO_4)_3 + NH_4SCN$.* $Cr_2(SO_4)_3 \cdot 18\ H_2O$ was employed in 10% solution in water. A crystal of NH_4SCN was employed as above.

37. *$NiSO_4 + NH_4SCN$.* $NiSO_4 \cdot 7\ H_2O$ was employed in 10% solution in water. A crystal of NH_4SCN was employed with the reagent as described above.

38. *$Na_3Co(NO_2)_6$.* The reagent was that employed in the test for potassium. It is prepared as follows:

H_2O	50 ml.	
$CoCl_2$	4 g.	
KNO_2	10 g.	
$HC_2H_3O_2$	2 ml.	Dilute to 100 ml.

39. *(A) K_2PdBr_4.*

$PdCl_2 \cdot 2\ H_2O$	5 g.
KBr	20 g.
H_2O	100 ml.

(B) $PdCl_2$ in HBr.

$PdCl_2 \cdot 2\ H_2O$	5 g.
10% HBr in H_2O	100 ml.

Since $PdCl_2$ has been useful, as described by *Stephenson*,[11] it was thought that the added bromide ions in the reagent might be of advantage.

[23] *C. C. Fulton*, Amer. J. Pharmac. **105**, 326, 374 (1933).

40. Na_2SnI_4. The formula for acid sodium stannous iodide, as described by *Fulton*,[16] was employed:

"Treat 3 g. tin with 25 ml. conc. HCl. When evolution of hydrogen has apparently ceased add 75 ml. water and $^1/_2$ g. of excess tin. Keep this as a stock solution. The reagent itself will not keep long." For use, add 2 g. NaI to 4 ml. of the $SnCl_2$ solution.

V. Diazo Test

41. *Diazo reaction.* This is a color and precipitation reaction originally described by *Rosenthaler*.[24] A red color or precipitate is obtained when diazotized novocaine is coupled with alkaline beta naphthol. The reaction was performed to see if other alkaloids would give precipitation reactions under similar conditions. The details of the test are as follows: To one drop of the alkaloid solution, add one drop of 10% KNO_2, acidify with one drop of 1 to 3 *N* HCl. Then add one drop of 5% KOH containing a crystal (5 to 10 mg.) of beta naphthol.

Systematic Record of Microchemical Tests

For the tests reported in the following pages, ordinary microscope slides were used unless the necessity of employing organic solvents made it advisable to substitute cavity slides. One drop of the test solution, equivalent to about 0,02 ml. solution or 0,2 mg. of the alkaloid, was placed in the center of the slide. A drop of the reagent was placed close to the test drop, and the two solutions were then merged by drawing the tip of a glass rod from one drop to another. The result was observed under the microscope. If no crystals formed, the test was set aside and observed from time to time until finally all of the solvent evaporated. Occasionally the test drop was warmed to promote crystallization.

At times it was found useful to recrystallize a precipitate in order to obtain more useful test forms. If alcohol or some other organic solvent was to be used, the recrystallization was carried out in the depression of a cavity slide.

Beta Eucaine

The alkaloid, benzoyl vinyl-diacetone alkamine hydrochloride, was found to meet the standards for identity and purity of the United States Pharmacopeia X. A 1% solution of the beta eucaine in distilled water was employed for the following tests. The concentration corresponds to 10 mg. of the eucaine per milliliter of solution.

1. Br_2 *in* $NaBr$. A yellow oil forms.
2. ICl_3. A yellow oil forms.

[24] *L. Rosenthaler*, Toxikologische Mikroanalyse, Berlin 1935.

3. *(A)* $HClO_4$. No noticeable change occurs.
   (B) NH_4ClO_4. No change.
4. $Na_2B_4O_7$. A turbidity forms at once.
5. NH_4VO_3. No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* No change.
8. *Sodium veronalate.* No change.
9. *Cupferron.* No immediate precipitate appears, but on standing, a number of colorless, irregularly shaped crystals form. Some of these collect into groups with thin prisms growing out from the centers.

Birefringence	strong.
Extinction	oblique, but difficult to determine.
Elongation	negative.
Limiting concentration	10 mg./ml.
Illustration	figure 30.

10. *Potassium acid phthalate.* No change.
11. *KBr.* A large number of small colorless rhombs, squares and hexagonal plates are formed.

Birefringence	strong.
Extinction	parallel or symmetrical.
Elongation	indefinite.
Limiting concentration	5 mg./ml.
Crystal angle	82° (smallest angle on rhombs).
Illustration	figure 31.

12. *(A)* $SnCl_2$. Initially no change occurs, but after a few minutes a large number of symmetrical aggregates of prisms appear. They have rounded ends.

Birefringence	strong.
Extinction	oblique.
Elongation	negative.
Limiting concentration	10 mg./ml.
Illustration	figure 33.

(B) $SnBr_2$. Aggregates of the same appearance and constants similar to the above are obtained. The crystals, however, are smaller.
13. $TiCl_3$. No change occurs.
14. $BiCl_3$. No change occurs.
15. *Potassium antimonyl tartrate.* No change.
16. $AsCl_3$. No change.
17. *Mercurochrome.* A red precipitate is produced at once.
18. $NaAgI_2$. No change.
19. *(A)* $KAuI_2$. A heavy dark-colored turbidity forms at once.
    (B) $HAuI_2$. A heavy dark-colored turbidity forms at once.
20. *(A).* $NaAuBr_4$. No change occurs.
    (B) $HAuBr_4$. No change occurs.

21. $IrCl_4$. A few, brown, irregular, crystalline aggregates are formed on standing. These consist of dark-colored prismatic clusters. The individual branches are leaflike in appearance.

Dichroism	yellow to brown.
Birefringence	strong.
Extinction	oblique.
Elongation	positive.
Illustration	figure 61.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. No immediate precipitation occurs. However, on standing, and by scratching, golden-yellow aggregates of prisms form.

Birefringence	strong.
Extinction	oblique. (Shown in figure 69.)
Elongation	positive.
Illustration	figure 69.

25. *(A)* H_2PtCl_6 *in* 20% HBr. At first, no change is observed. On standing, oily droplets form along the edge of the test drop. A few of these crystallize into brilliantly anisotropic flowerlike aggregates.

(B) H_2PtCl_6 *in* 5% HBr. An amorphous precipitate is formed. On standing, a number of clusters of leaflike prisms develop. If the original, amorphous precipitate from 0,5% solution is warmed and stirred, the unit crystals are obtained. They consist of rhombs and six and eightsided prisms.

Birefringence	strong.
Extinction	prisms oblique, angle approximately 34°; rhombs symmetrical.
Elongation	rhombs, negative along the longer diagonal.
Limiting concentration	5 mg./ml.
Illustration	figure 76.

26. K_2PtI_6. A heavy, dark-colored precipitate is obtained at once.

27. Cs_2CdI_4. Oily drops appear on standing.

28. *(A)* CdI_2. An amorphous precipitate forms.

(C) $Cd(NO_3)_2 + NH_4SCN$. A colorless turbidity develops.

29. *(A)* K_2HgBr_4. An oily turbidity forms immediately.

(B) K_2HgBr_4, *acidified*. With stirring and scratching, a large number of colorless rhombs appear. Some larger clusters of pointed prisms grow on standing. If the test drop is warmed a great many thin four and six-sided prisms form, with a few arranging themselves into clusters. These recrystallize well from alcohol.

Birefringence	weak.
Extinction	rhombs symmetrical. prisms oblique, average of 32°.
Elongation	prisms positive.
Limiting concentration	1 mg./ml.
Illustration	figure 106.

30. $K_2Hg(SCN)_4$. A colorless oily precipitate appears.

31. *Potassium thallic iodide.* A heavy, yellowish-red, amorphous precipitate is formed directly.

32. *(A)* H_2SnCl_6. On allowing the test drop to evaporate almost to dryness, very large groups of overlapping blades are formed, growing out from a common center. This is a characteristic test form.

Birefringence	strong.
Extinction	oblique, approximately 16°.
Elongation	negative.
Limiting concentration	10 mg./ml.
Illustration	figure 111.

(B) $H_2SnCl_6 + KBr$. Crystals similar to the above are produced although smaller. The branching blades are more dendritic in character.

Optical data	similar to the above.
Limiting concentration	5 mg./ml.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. A colorless oily turbidity.

35. $Co(NO_3)_2 + NH_4SCN$. No change.

36. $Cr_2(SO_4)_3 + NH_4SCN$. A turbidity forms.

37. $NiSO_4 + NH_4SCN$. A turbidity forms.

38. $Na_3Co(NO_2)_6$. A turbidity forms.

39. *(A)* K_2PdBr_4. An immediate precipitation occurs which yields, on standing, a few leafy red aggregates. These are not always easily obtained. If the amorphous precipitate is warmed, quite a few clusters of pointed prisms are formed.

Dichroism	yellow to brown.
Birefringence	weak.

(B) $PdCl_2$ *in* HBr. Clusters of pointed prisms are formed on warming. Crystallization is better than in A. Optical data are the same.

40. Na_2SnI_4. A light-colored precipitate forms.

41. *Diazo test.* No change.

Characteristic Test Forms

Beta eucaine gives a number of crystalline complex salts. These salts are formed, in general, with the same reagents that yield insoluble crystalline compounds with cocaine. Fortunately—since the eucaine is used as a cocaine substitute—the derivatives of the latter differ in appearance and optical characteristics from those of eucaine. The best test form for identification of beta eucaine is the platinic bromide complex in conjunction with its optical properties. Cupferron is a very specific reagent, beta eucaine being the only alkaloid studied which gives a crystalline derivative with this reagent.

Cocaine

The alkaloid used in these tests was found to meet the standards of purity of the United States Pharmacopeia X. A one per cent solution of the alkaloid salt in distilled water was employed for the following tests. This gave a solution containing 9 mg. of cocaine base per milliliter.

1. *Br_2 in NaBr.* A yellow oil is formed immediately.
2. *ICl_3.* An oil is formed at once.
3. *(A) $HClO_4$.* A slight precipitate forms; on standing, fairly large transparent branching crystals develop. These are composed of dendritic prisms and rhombs which occasionally occur singly.

Birefringence	weak.
Extinction	parallel on prisms.
Elongation	negative.
Limiting concentration	10 mg./ml.
Illustration	figure 10.

(B) NH_4ClO_4. Symmetrical spherulites of thin needles are formed in the solution.

Optical constants	as above.
Limiting concentration	2 mg./ml.
Illustration	figure 14.

4. *$Na_2B_4O_7$.* A white precipitate is formed. Addition of a drop of alcohol yields a few pointed crystals.
5. *NH_4VO_3.* No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* A colorless turbidity results.
8. *Sodium veronalate.* On standing, oily drops appear.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.
11. *KBr.* No change.
12. *(A) $SnCl_2$.* If the precipitate first formed is warmed, irregular spheres and a few separate, stubby prisms result.

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Limiting concentration	10 mg./ml.

(B) $SnBr_2$. There are produced immediately, from an amorphous precipitate, large aggregates of fine colorless needles. They yield a polarization cross under crossed nicols.

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Limiting concentration	5 mg./ml.

13. $TiCl_3$. No change.

14. $BiCl_3$. No change.

15. *Potassium antimonyl tartrate.* No change.

16. $AsCl_3$. No change.

17. *Mercurochrome.* A heavy, red precipitate is produced immediately.

18. $NaAgI_2$. Colorless clusters of pointed, irregularly-shaped blades soon develop. This reaction, first observed by *Fulton*,[23] is a beautiful and characteristic one.

Birefringence ..... strong.
Extinction ..... oblique, approx. 40°.
Elongation ..... positive.
Limiting concentration ..... 2 mg./ml.
Illustration ..... figure 46.

19. *(A)* $KAuI_2$. A dark-colored amorphous precipitate results.
(B) $HAuI_2$. A dark-colored amorphous precipitate results.

20. *(A)* $NaAuBr_4$. The reagent forms a crystalline precipitate similar to that with $HAuCl_4$ described by *Amelink*.[12] The bromide, however, is more sensitive. The initial amorphous precipitate soon crystallizes. The crystals consist of overlapping prisms joined together in skeletal form, sometimes in groups with three or four main branches. Alcohol is useful for recrystallization. Likewise warming often promotes crystallization. If to a 0,1% solution of the alkaloid, the reagent is added an then stirred, the unit forms of the aggregate are found to be chiefly thin rhombs and unsymmetrical hexagonal plates.

Dichroism ..... yellowish-brown to brown.
Birefringence ..... strong.
Extinction ..... hexagonal plates oblique, 9°; rhombs symmetrical.
Elongation ..... rhombs negative along long diagonal; hexagonal plates negative.
Limiting concentration 0,5 mg./ml.

(B) $HAuBr_4$. The reagent yields results similar to the above.

Illustration ..... figure 54.

21. $IrCl_4$. Long brown branching crystals appear, similar to the chlorplatinate of *Stephenson*,[11] but not so featherlike.

Illustration ..... figure 62.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change is observed at first, but on standing, small crystals appear singly and in pairs. They consist of serrated prisms joined together so they appear bent at the center.

Birefringence ..... weak.
Extinction ..... oblique, approx. 20°.
Elongation ..... negative.
Limiting concentration ..... 10 mg./ml.
Illustration ..... figure 120.

24. Na_2OsCl_6. A thick mass of long slender yellow crystals forms at once. They are composed of stems with branches not quite at right angles. The branches are shorter than those in the chlorplatinate of *Stephenson*.[11] This precipitate is not as valuable for purposes of identification as the platinic bromide.

Illustration ..... figure 70.

25. *(A)* H_2PtCl_6 *in* 20% HBr. A precipitate of deep-yellow branching twiglike crystals is immediately formed. They are similar to the chlorplatinate of *Stephenson* except that the crystalline forms are somewhat larger and heavier, not so featherlike in appearance.

(B) H_2PtCl_6 *in* 5% HBr. Yellow, branching featherlike crystals are obtained, which on standing disintegrate into twiglike crystals.

Birefringence ..... weak.
Extinction ..... oblique, approx. 18°.
Elongation ..... positive.
Limiting concentration ..... 0,3 mg./ml.
Illustration ..... figure 77.

26. K_2PtI_6. A dark-colored amorphous precipitate results.
27. Cs_2CdI_4. A colorless amorphous precipitate is obtained.
28. *(A)* CdI_2. A colorless amorphous precipitate is obtained.
(B) $CdBr_2$. An amorphous precipitate forms.
(C) $Cd(NO_3)_2 + NH_4SCN$. An amorphous precipitate forms.
(D) $CdCl_2$. No change.
29. *(A)* K_2HgBr_4. A white precipitate forms at once.
(B) K_2HgBr_4, *acidified*. A white precipitate forms at once.
30. $K_2Hg(SCN)_4$. A turbidity forms at once.
31. *Potassium thallic iodide*. A dark-colored precipitate results.
32. *(A)* H_2SnCl_6. On standing, a number of wedge-shaped crystals appear. A few of these collect into irregular aggregates.

Birefringence ..... strong.
Extinction ..... parallel and oblique.
Elongation ..... positive.
Limiting concentration ..... 10 mg./ml.
Illustration ..... figure 112.

(B) $H_2SnCl_6 + KBr$. Crystals similar to the above are obtained. The aggregates are more common in this case. The test is more sensitive than when the chlorstannic acid alone is employed. Optical data are similar to those in (A).

33. $HSbCl_4$. No change.
34. $MnSO_4 + NH_4SCN$. A colorless oil results.
35. $Co(NO_3)_2 + NH_4SCN$. A blue oil results.
36. $Cr_2(SO_4)_3 + NH_4SCN$. An oil forms at once.

37. $NiSO_4 + NH_4SCN$. An oil forms at once.

38. $Na_3Co(NO_2)_6$. A turbidity forms at once.

39. *(A)* K_2PdBr_4. An orange-colored precipitate results.

(B) $PdCl_2$ *in HBr*. Results are as in (A).

40. Na_2SnI_4. "Rosettes of delicate branching needles" as described by *Fulton*.[23]

Birefringence	weak.
Extinction	difficult to obtain.
Elongation	positive.
Illustration	figure 131.

41. *Diazo test*. No change.

Characteristic Test Forms

The alkaloid cocaine gives a number of crystalline derivatives, the most characteristic of which is the precipitate with sodium silver iodide. No other alkaloids studied give crystals with this reagent with the exception of brucine and strychnine, whose crystals are probably the simple iodides and can easily be distinguished from the cocaine precipitate. The ruthenium double salt is likewise only given by these other two alkaloids whose crystalline forms are again different. The chlorplatinic acid in 5% HBr is a much more sensitive and useful reagent for cocaine than the simple chlorplatinic acid. In fact, it may be noted that by increasing the content of sodium bromide in the chlorplatinic acid solution to twice or three times the normal amount, an unusual limiting concentration of about 0,3 mg./ml. is obtained.

Novocaine

The novocaine (procaine hydrochloride) employed for the following tests was found to meet the standards of purity of the United States Pharmacopeia X. The alkaloid was used in 1% solution in distilled water. This gave a solution containing 10 mg. of novocaine per milliliter of solution.

1. Br_2 *in* $NaBr$. One obtains, almost immediately, as observed by *Fulton*,[23] white rosettes of prisms and needles. These enlarge on standing to yellowish-colored overlapping prismatic clusters. On standing, the rosettes tend to disintegrate.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Limiting concentration	0,5 mg./ml.
Illustration	figure 1.

2. ICl_3. A yellow turbidity forms.

3. *(A)* $HClO_4$. No change.

(B) NH_4ClO_4. On warming and scratching the test drop, many rhombs and elongated pointed prisms develop. *Rosenthaler*[24] describes a similar precipitate from 2% alkaloid solution using $NaClO_4$. He gives the principal prism angle of 74°.

Birefringence	strong.
Extinction	symmetrical on rhombs; prisms oblique, average of 32°.
Elongation	prisms negative.
Limiting concentration	10 mg./ml.
Illustration	figure 13.

4. $Na_2B_4O_7$. A turbidity forms.
5. NH_4VO_3. No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* A turbidity forms.
8. *Sodium veronalate.* On standing, a slight turbidity forms.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.
11. *KBr.* No change.
12. $SnCl_2$. No change.
13. $TiCl_3$. No change.
14. $BiCl_3$. No change.
15. *Potassium antimonyl tartrate.* No change.
16. $AsCl_3$. No change.
17. *Mercurochrome.* A red precipitate forms at once.
18. $NaAgI_2$. No change.
19. *(A)* $KAuI_2$. A dark-colored precipitate forms, from which, on standing, crystals similar to those with $HAuI_2$ result.

(B) $HAuI_2$. A dark, oily precipitate results which, on concentration by evaporation, forms large groups of dendritic needles with some symmetrical spherulites.

Dichroism	light-brown to dark-brown.
Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	2 mg./ml.
Illustration	figure 47.

20. *(A)* $NaAuBr_4$. A red precipitate forms, from which, on warming and stirring, clusters of pointed prisms are obtained. The crystals are small and best observed with a magnification of 200 ×. Optical properties are similar to those of the crystals obtained with $HAuBr_4$.

(B) $HAuBr_4$. On warming and stirring, aggregates of prisms similar to the above are observed.

Dichroism	yellow to orange.
Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	0,5 mg./ml.
Illustration	figure 55.

21. $IrCl_4$. A dark-colored amorphous precipitate results.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. No change.

25. *(A)* H_2PtCl_6 *in 20% HBr.* A slight amorphous precipitate results.

(B) H_2PtCl_6 in 5% *HBr.* The solution remains clear. However, if just a trace of the reagent be added to a drop of the alkaloid test solution, one immediately gets red dendritic serrated aggregates of crystals, with a few symmetrical spherulites and fernlike growths. Scratching the slide aids in crystal formation.

Illustration	figure 78.

(C) Na_2PtBr_6. Using just a trace of reagent as outlined above, fernlike forms and spherulites result. The novocaine platino bromides polarize very little and too irregularly for optical characterization.

Limiting concentration	3 mg./ml.

26. K_2PtI_6. A dark-colored oil is produced at once.

27. $CsCdI_4$. A few oily drops appear on standing.

28. *(A)* CdI_2. A colorless amorphous precipitate forms.

(B) $CdBr_2$. A crystalline precipitate of small colorless rectangular plates and of branching dendritic aggregates of overlapping plates is immediately formed. The crystals have a low refractive index and are better observed with crossed nicols. The ends are rectangular or slightly slanting.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	2 mg./ml.
Illustration	figure 94.

(C) $Cd(NO_3)_2 + NH_4SCN$. No change.

(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. A precipitate results at once.

(B) K_2HgBr_4, *acidified.* A precipitate results at once.

30. $K_2Hg(SCN)_4$. A turbidity is produced.

31. *Potassium thallic iodide.* A red turbidity is produced.

32. H_2SnCl_6. No change.

33. $HSbCl_4$. No change.
34. $MnSO_4 + NH_4SCN$. A turbidity forms.
35. $Co(NO_3)_2 + NH_4SCN$. A turbidity forms. It is colored blue.
36. $Cr_2(SO_4)_3 + NH_4SCN$. A turbidity forms.
37. $NiSO_4 + NH_4SCN$. A green oil forms on standing.
38. $Na_3Co(NO_2)_6$. A slight turbidity forms.
39. *(A)* K_2PdBr_4. An orange precipitate results.
(B) $PdCl_2$ *in* HBr. No change.
40. Na_2SnI_4. On warming and stirring, the initial precipitate yields aggregates of short, rectangular prisms as mentioned by *Fulton*.[23] The prisms polarize well but the individual crystals are not suitable for optical characterization.

Illustration ..... figure 132.

41. *Diazo reaction.* An orange-red color results on coupling with beta naphthol. This test is described by *Rosenthaler*.[22]

Characteristic Test Forms

Novocaine yields a considerable number of precipitates with the reagents employed. Crystalline derivatives are not very numerous. The most characteristic crystalline precipitate is that with Br_2 in KBr. Next in order of usefulness, are the iodoauric and bromauric acid salts. Finally, the cadmium bromide crystals are of some interest. The color reaction with beta naphthol is not given by any of the other nineteen alkaloids tested.

Stovaine

A 1% solution of the hydrochloride of dimethyl-amino methyl butanol benzoate, "Poulenc Frères", Paris, was prepared with distilled water. This gave a solution containing 10 mg./ml. of stovaine. The gold chloride and picrolonic acid derivatives were identical with those described by *Amelink*.[12]

1. Br_2 *in* KBr. A yellow turbidity forms.
2. ICl_3. A yellow turbidity forms.
3. *(A)* $HClO_4$. No change.
(B) $NaClO_4$. No change.
4. $Na_2B_4O_7$. A turbidity results.
5. NH_4VO_3. No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* A turbidity results.
8. *Sodium veronalate.* A turbidity results.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.

11. *KBr.* The test drop remains clear. After concentration by evaporation and then scratching the slide, a number of thin oblong plates appear, overlapping and sometimes collecting into clusters.

Birefringence ..... weak.
Extinction ..... parallel.
Elongation ..... not definite.
Illustration ..... figure 32.

12. $SnCl_2$. No change.
13. $TiCl_3$. No change.
14. $BiCl_3$. No change.
15. *Potassium antimonyl tartrate.* No change.
16. $AsCl_3$. No change.
17. *Mercurochrome.* A red precipitate forms at once.
18. $NaAgI_2$. No change.
19. *(A)* $KAuI_2$. A black precipitate results.
(B) $HAuI_2$. A black precipitate results.
20. *(A)* $NaAuBr_4$. One gets a blood-red amorphous precipitate, from which, very shortly, are obtained fine interlacing clusters of needles. If a drop of alcohol be added to these crystals, small hexagonal plates and rhombs, some with rounded edges, are formed.

Dichroism ..... yellow to brown.
Birefringence ..... weak.
Extinction ..... parallel.
Elongation ..... plates negative.
Limiting concentration ..... 0,5 mg./ml.

(B) $HAuBr_4$. A dark-red precipitate is produced. On standing or warming, a number of large needle-like crystals appear from the amorphous mass. Larger forms of bevel-ended prisms occur. Some have notched ends.

Optical properties are the same as those in (A).
Illustration ..... figure 56.

21. $IrCl_4$. The test drop remains clear.
22. $RhCl_3$. The test drop remains clear.
23. $RuCl_3$. The test drop remains clear.
24. Na_2OsCl_6. No change.
25. *(A)* H_2PtCl_6 *in 20% HBr.* An orange-colored precipitate forms.
(B) H_2PtCl_6 in *5% HBr.* An orange-colored precipitate forms.
(C) Na_2PtBr_6. An orange-colored precipitate forms.
26. K_2PtI_6. A dark-colored precipitate forms immediately and in large quantity.
27. Cs_2CdI_4. An oily turbidity is produced at once.
28. *(A)* CdI_2. An oily turbidity is produced at once.
(B) $CdBr_2$. No change.

(C) $Cd(NO_3)_2 + NH_4SCN$. A turbidity results.

(D) $CdCl_2$. No change.

29. (A) K_2HgBr_4. A turbidity results.

(B) K_2HgBr_4, *acidified*. A turbidity results.

30. $K_2Hg(SCN)_4$. A turbidity results.

31. *Potassium thallic iodide*. A bulky reddish-brown precipitate results at once.

32. (A) H_2SnCl_6. No change.

(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. A turbidity forms.

35. $Co(NO_3)_2 + NH_4SCN$. A turbidity forms.

36. $Cr_2(SO_4)_3 + NH_4SCN$. A turbidity forms.

37. $NiSO_4 + NH_4SCN$. A turbidity forms.

38. $Na_3Co(NO_2)_6$. An orange-colored oil forms.

39. (A) K_2PdBr_4. A bulky brown precipitate is formed at once.

(B) $PdCl_2$ *in* HBr. A bulky brown precipitate is formed at once.

40. Na_2SnI_4. No change.

41. *Diazo test*. No change.

Characteristic Test Forms

Stovaine gives a large number of precipitates with the alkaloid reagents. However, relatively few of these tend to crystallize. The gold bromide complexes are most useful for purposes of identification especially when recrystallized from alcohol. The crystalline phase obtained on standing with the KBr reagent is an interesting test form.

Cinchonine

The test solution was prepared by dissolving 100 mg. of the cinchonine base in 0,1 *N* HCl and diluting the solution to 10 ml. with distilled water, which gives a solution containing 10 mg. of the base per milliliter. The alkaloid used was tested for purity and was found to meet the standards of the U. S. Pharmacopeia X.

1. Br_2 *in* $NaBr$. A yellow amorphous precipitate forms.

2. ICl_3. A copious yellow precipitate forms at once.

3. (A) $HClO_4$. The test drop remains clear.

(B) NH_4ClO_4. On standing for some time, many rectangular prisms, with occasional wedge-shaped forms and rhombs, appear.

Birefringence	strong.
Extinction	parallel and symmetrical on rhombs.
Elongation	positive.
Limiting concentration	10 mg./ml.
Illustration	figure 15.

4. $Na_2B_4O_7$. The free base is obtained in needle-like aggregates without difficulty. Some exhibit a polarization cross.

Birefringence	weak.
Extinction	difficult to establish.
Elongation	positive.
Illustration	figure 18.

5. NH_4VO_3. A yellow precipitate forms at once.

6. *Potassium anthraquinone sulfonate.* A slight precipitate results.

7. *Potassium xanthate.* A turbidity results.

8. *Sodium veronalate.* An oily precipitate results at first. On standing, however, a number of spheres composed of small yellow needles develop. This is probably the free base. Constants are the same as those reported in test No. 4.

9. *Cupferron.* A pronounced turbidity is produced.

10. *Potassium acid phthalate.* A turbidity results at once.

11. KBr. No change.

12. *(A)* $SnCl_2$. No change.
(B) $SnBr_2$. No change.

13. $TiCl_3$. A slight turbidity results on standing.

14. $BiCl_3$. No change.

15. *Potassium antimonyl tartrate.* No change.

16. $AsCl_3$. No change.

17. *Mercurochrome.* A heavy red non-crystalline precipitate forms at once.

18. $NaAgI_2$. No change.

19. *(A)* $KAuI_2$. A dark-colored precipitate is produced.
(B) $HAuI_2$. A dark-colored precipitate is produced.

20. *(A)* $NaAuBr_4$. A red amorphous precipitate is formed.
(B) $HAuBr_4$. A red amorphous precipitate is formed.

21. $IrCl_4$. No change.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. From the yellow precipitate first obtained, there are formed rather unsymmetrical aggregates of pointed prisms. The units of the group are composed of four and six-sided thin plates. The precipitate is insoluble in alcohol.

Birefringence	weak.
Extinction	parallel and oblique.
Elongation	negative.
Limiting concentration	10 mg./ml.
Illustration	figure 71.

25. *(A)* H_2PtCl_6 *in 20% HBr.* There results immediately an orange precipitate composed of small needles and pointed prisms. A few yellowish

dendritic aggregates are obtained, especially if the test solution be more concentrated than 1%.

Dichroism ..... yellow to orange.
Birefringence ..... weak.
Extinction ..... oblique.
Elongation ..... negative.
Limiting concentration ..... 0,1 mg./ml.
Illustration ..... figure 79.

(B) H_2PtCl_6 *in 5% HBr.* Results similar to the above are obtained.

(C) Na_2PtBr_6. Results similar to the above are obtained.

26. K_2PtI_6. A dark-colored amorphous precipitate results at once, from which one obtains, on standing, clusters of dark, serrated, overlapping prisms. They do not transmit light.

Limiting concentration ..... 0,1 mg./ml.

27. Cs_2CdI_4. A slight precipitate forms.

28. *(A)* CdI_2. A slight precipitate forms.

(B) $CdBr_2$. No change.

(C) $Cd(NO_3)_2 + NH_4SCN$. A turbidity is produced.

29. *(A)* K_2HgBr_4. A heavy white precipitate results.

(B) K_2HgBr_4. *acidified.* A rather slight precipitate forms.

30. $K_2Hg(SCN)_4$. A heavy oil is formed in the solution.

31. *Potassium thallic iodide.* A heavy red precipitate is thrown down at once.

32. *(A)* H_2SnCl_6. No change.

(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. One obtains usually, a number of prisms of high refractive index. They are long and pointed and also hexagonal in shape. These are forms of the simple cinchonine thiocyanate.

Birefringence ..... strong.
Extinction ..... parallel and oblique.
Elongation ..... negative.

35. $Co(NO_3)_2 + NH_4SCN$. A blue-colored turbidity results.

36. $Cr_2(SO_4)_3 + NH_4SCN$. A turbidity forms.

37. $NiSO_4 + NH_4SCN$. The simple cinchonine thiocyanate is obtained as in 34.

38. $Na_3Co(NO_2)_6$. An orange-colored turbidity is produced at once.

39. *(A)* K_2PdBr_4. An orange-colored turbidity is produced at once.

(B) $PdCl_2$ *in HBr.* An orange-colored turbidity is produced at once.

40. Na_2SnI_4. No change.

41. *Diazo reaction.* No change.

Characteristic Test Forms

The platinic bromide complex in conjunction with its optical properties is most characteristic for cinchonine. The perchlorate crystals are useful but not as easily obtained. The platinic iodide precipitate is useful since this reagent gives relatively few crystalline precipitates. The unusually low limiting concentration of the test recommends its use for identification of very small amounts of the alkaloid.

Cinchonidine

The test solution was prepared by dissolving 0.127 g. of cinchonidine sulfate, $(C_{10}H_{22}ON_2)_2 \cdot H_2SO_4 \cdot 3\,H_2O$, in 10 ml. of distilled water which gives a solution containing 10 mg. of anhydrous alkaloid base per milliliter. The alkaloid used was tested for purity and was found to meet the standards of the U. S. Pharmacopeia X.

1. *Br_2 in NaBr.* A yellow amorphous precipitate results at once.
2. *ICl_3.* A yellow amorphous precipitate results at once.
3. *(A) $HClO_4$.* No change.
   (B) NH_4ClO_4. No change.
4. *$Na_2B_4O_7$.* An oil is first observed, from which one obtains, in two or three minutes, a number of spherical aggregates similar to the free base. Recrystallization by addition of a drop of alcohol yields the hexagonal prisms reported by *Amelink*.[12]

Birefringence	weak, a good polarization cross results.
Extinction	parallel on prisms.
Elongation	positive.
Illustration	figure 19, aggregates under crossed nicols.

5. *NH_4VO_3.* A light yellow-colored amorphous precipitate is produced at once.
6. *Potassium anthraquinone sulfonate.* A number of aggregates of dense colorless needles form on standing a few minutes or on warming the initial precipitate.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 26.

7. *Potassium xanthate.* An oil separates.
8. *Sodium veronalate.* No change.
9. *Cupferron.* A colorless amorphous precipitate results.
10. *Potassium acid phthalate.* No change.
11. *KBr.* No change.
12. *$SnCl_2$.* No change.
13. *$TiCl_3$.* No change.

14. $BiCl_3$. No change.

15. *Potassium antimonyl tartrate.* No change.

16. $AsCl_3$. No change.

17. *Mercurochrome.* A voluminous red precipitate is formed immediately.

18. $NaAgI_2$. No change.

19. *(A)* $KAuI_2$. A dark-colored precipitate results at once.
(B) $HAuI_2$. A dark-colored precipitate results at once.

20. *(A)* $NaAuBr_4$. A amorphous precipitate results.
(B) $HAuBr_4$. An amorphous precipitate results.

21. $IrCl_4$. A reddish-brown precipitate is formed at once, from which there appear in great numbers dark-colored aggregates of pointed prismatic forms.

Birefringence	weak.
Extinction	parallel.
Elongation	positive.
Illustration	figure 63.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. There are formed, almost at once, sheaves and clusters of branching needle-like prisms. They are colored yellow.

Birefringence	weak.
Extinction	parallel.
Elongation	positive.
Illustration	figure 72.

25. *(A)* H_2PtCl_6 *in 20% HBr.* A yellow precipitate appears immediately. It is composed of irregular needles singly and in groups and sheaves. The needles have serrated edges.

Birefringence	weak.
Extinction	parallel.
Elongation	positive.
Limiting concentration	1 mg./ml.
Illustration	figure 80.

(B) H_2PtCl_6 *in 5% HBr.* Results similar to the above are obtained.

(C) Na_2PtBr_6. Results similar to the above are obtained.

26. K_2PtI_6. A dark-colored precipitate is formed. Using a drop of glycerol between the test drop and the drop of reagent, there are noted a large number of small dark needles as the reagents mix through the glycerol. In dilute solution, crystals result directly in the aqueous test solution.

Limiting concentration	0,05 mg./ml.
Illustration	figure 90.

27. Cs_2CdI_4. A colorless non-crystalline precipitate results.

28. *(A)* CdI_2. A colorless non-crystalline precipitate results.
(B) $CdBr_2$. A colorless non-crystalline precipitate results.
(C) $Cd(NO_3)_2 \cdot NH_4SCN$. A non-crystalline precipitate results.
(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. A colorless amorphous precipitate forms at once.
(B) K_2HgBr_4, *acidified*. A colorless amorphous precipitate forms at once.

30. $K_2Hg(SCN)_4$. An amorphous precipitate results.

31. *Potassium thallic iodide*. A dark-colored precipitate forms.

32. *(A)* H_2SnCl_6. No change.
(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. A turbidity results.

35. $Co(NO_3)_2 + NH_4SCN$. A turbidity forms.

36. $Cr_2(SO_4)_3 + NH_4SCN$. A turbidity forms.

37. $NiSO_4 + NH_4SCN$. A turbidity forms.

38. $Na_3Co(NO_2)_6$. A yellow amorphous precipitate forms immediately.

39. *(A)* K_2PdBr_4. An orange-colored precipitate results.
(B) $PdCl_2$ *in HBr*. An orange-colored precipitate results.

40. Na_2SnI_4. A precipitate forms immediately and, on warming, spherulites of prisms result.

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Limiting concentration	1 mg./ml.
Illustration	figure 133.

41. *Diazo reaction*. No change.

Characteristic Test Forms

The main group of the platinum metals—osmium, iridium, and platinum—yields characteristic tests with cinchonidine. Although these do not differ greatly in crystalline form, the chlorosmate is the most convenient as to size, solubility, and determination of optical constants. The crystals obtained with tin iodide are most useful for the identification of cinchonidine because of the relatively few alkaloids that give crystalline precipitates with this reagent.

Quinidine

The test solution was prepared by dissolving 0,121 g. quinidine sulfate U. S. P. in 10 ml. of distilled water which gives a solution containing 10 mg. of the alkaloid base per milliliter. The alkaloid salt used was tested for purity and was found to meet the standards of the U. S. Pharmacopeia X.

1. Br_2 *in* $NaBr$. A yellow turbidity forms.
2. ICl_3. Yellow, irregular amorphous masses form.
3. *(A)* $HClO_4$. A slight precipitate is obtained.
(B) NH_4ClO_4. Well formed triangular crystals result. Some of these collect into irregular aggregates with serrated edges.

Birefringence	weak.
Extinction	parallel and symmetrical.
Elongation	positive, along bisector of principal angle (74°).
Illustration	figure 16.

4. $Na_2B_4O_7$. A turbidity is produced but no crystals form. However, a drop of alcohol added to the test drop produces at once a good crop of long pointed needles.

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Illustration	figure 20.

5. NH_4VO_3. A yellow amorphous precipitate forms at once.
6. *Potassium anthraquinone sulfonate.* There soon results a large number of colorless, well-formed prisms, many of them with notched ends. On standing, they grow thicker, with pointed tops growing up from the simple prisms. The refractive index of the prisms is low, so they are best observed under crossed nicols.

Birefringence	good.
Extinction	parallel.
Elongation	negative.
Limiting concentration	1 mg./ml.
Illustration	figure 27.

7. *Potassium xanthate.* An amorphous precipitate forms at once.
8. *Sodium veronalate.* A turbidity forms.
9. *Cupferron.* A colorless precipitate is obtained at once.
10. *Potassium acid phthalate.* A copious colorless precipitate forms.
11. KBr. No change.
12. *(A)* $SnCl_2$. No change.
(B) $SnBr_2$. No change.
13. $TiCl_3$. No change.
14. $BiCl_3$. No change.
15. *Potassium antimonyl tartrate.* No change.
16. $AsCl_3$. No change.
17. *Mercurochrome.* A red precipitate results immediately.
18. $NaAgI_2$. No characteristic crystals are obtained. A few crystals occasionally result similar to those obtained with sodium iodide alone.

The quinidine iodide has been described by *Behrens-Kley*.[25] It consists of small triangular plates, hexagonal prisms and rhombs.

Birefringence ..... good, except for the triangular forms.
Extinction ..... parallel on elongated forms.
Elongation ..... negative on elongated forms.

19. *(A)* $KAuI_2$. A black turbidity results.
(B) $KAuI_2$, *acidified*. A black turbidity results.

20. *(A)* $NaAuBr_4$. A red precipitate forms; on warming, it gives red oily drops. From these one gets small prisms, singly, in rosettes, and in sheaves (stirring is sometimes advisable). The crystalline form of the quinidine gold bromide has been described by *Rosenthaler*.[24] Crystals result most readily in about 0,5% solution of the alkaloid.

Dichroism ..... yellow to brown.
Extinction ..... parallel.
Elongation ..... positive.
Limiting concentration ..... 0,3 mg./ml.
Illustration ..... figure 58.

(B) $HAuBr_4$. The results obtained are the same as with (A).

21. $IrCl_4$. No change.
22. $RhCl_3$. No change.
23. $RuCl_3$. No change.
24. Na_2OsCl_6. No change.
25. *(A)* H_2PtCl_6 *in 20% HBr*. A yellow amorphous precipitate results.
(B) H_2PtCl_6 *in 5% HBr*. A yellow amorphous precipitate results.
(C) Na_2PtBr_6. A yellow amorphous precipitate results.
26. K_2PtI_6. A copious dark-colored precipitate is obtained.
27. Cs_2CdI_4. A colorless precipitate forms at once.
28. *(A)* CdI_2. A colorless precipitate forms at once.
(B) $CdBr_2$. No change.
(C) $Cd(NO_3)_2 + NH_4SCN$. Crystals similar to the simple quinidine thiocyanate are formed. The crystalline form of this salt is described by *Rosenthaler*.[24] As precipitated with solid NH_4SCN, fine colorless irregular branching clumps of needles result. These grow and separate, on standing, into six-sided plates.

Birefringence ..... strong.
Extinction ..... parallel.
Elongation ..... negative.

(D) $CdCl_2$. No change.

[25] *H. Behrens-P. D. C. Kley*, Organische mikrochemische Analyse, Leipzig 1922.

29. *(A)* K_2HgBr_4. A colorless amorphous precipitate forms at once.
(B) K_2HgBr_4, *acidified*. A colorless amorphous precipitate forms at once.

30. $K_2Hg(SCN)_4$. A copious colorless precipitate forms at once. Occasionally, crystals similar to the simple quinidine thiocyanate are obtained.

31. *Potassium thallic iodide*. A dark-colored amorphous precipitate forms at once.

32. *(A)* H_2SnCl_6. No change.
(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. Crystals similar to the simple quinidine thiocyanate are formed.

35. $Co(NO_3)_2 + NH_4SCN$. Quinidine thiocyanate crystals are obtained as described under 28.

36. $Cr_2(SO_4)_3 + NH_4SCN$. The quinidine thiocyanate crystals form.

37. $NiSO_4 + NH_4SCN$. The quinidine thiocyanate crystals form.

38. $Na_3Co(NO_2)_6$. A yellow-colored precipitate results at once.

39. *(A)* K_2PdBr_4. A copious orange precipitate is obtained.
(B) $PdCl_2$ *in* HBr. An orange precipitate is obtained.

40. Na_2SnI_4. A brown amorphous precipitate results.

41. *Diazo reaction*. No change.

Characteristic Test Forms

The most useful and characteristic reaction for quinidine obtained in these tests is the one with potassium anthraquinone sulfonate. The large, well-formed crystals of the sulfonate can easily be distinguished from the crystals of other precipitates obtained with this reagent. The quinidine perchlorate, in conjunction with its optical properties is a characteristic derivative.

Quinine

The test solution was prepared by dissolving 0.122 g. quinine dihydrochloride U. S. P. in 10 ml. of water, which gives a solution containing 10 mg. of the alkaloid base per milliliter. The quinine used met the standards of purity of the U. S. Pharmacopeia X.

1. Br_2 *in* $NaBr$. A yellow amorphous precipitate forms at once.
2. ICl_3. A colorless precipitate is formed immediately.
3. *(A)* $HClO_4$. No change.
(B) NH_4ClO_4. No change.
4. $Na_2B_4O_7$. A copious turbidity forms at once.
5. NH_4VO_3. A yellow precipitate forms at once.

6. *Potassium anthraquinone sulfonate.* A light-brownish colored precipitate is formed; from this, on standing, yellow sheaves and spherulites of needles grow. A polarization cross is obtained on the spherulites under crossed nicols.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 28.

7. *Potassium xanthate.* A white precipitate is produced.

8. *Sodium veronalate.* A turbidity forms.

9. *Cupferron.* No change.

10. *Potassium acid phthalate.* A colorless amorphous precipitate results.

11. *KBr.* No change.

12. *(A)* $SnCl_2$. No change.
(B) $SnBr_2$. No change.

13. $TiCl_3$. No change.

14. $BiCl_3$. No change.

15. *Potassium antimonyl tartrate.* No change.

16. $AsCl_3$. No change.

17. *Mercurochrome.* A heavy red precipitate appears at once.

18. $NaAgI_2$. A heavy dark-colored precipitate appears immediately.

19. *(A)* $KAuI_2$. A heavy dark-colored precipitate appears immediately.
(B) $HAuI_2$. A heavy dark-colored precipitate appears immediately.

20. *(A)* $NaAuBr_4$. An orange-colored precipitate forms immediately.
(B) $HAuBr_4$. An orange-colored precipitate forms immediately.

21. $IrCl_4$. A brown amorphous precipitate forms.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. No change.

25. *(A)* H_2PtCl_6 *in 20% HBr.* A voluminous orange precipitate is obtained, but no crystals. However, if quinine sulfate in 1% solution in 0,5 *N* HCl be employed, a crystalline phase is produced very soon from the initial amorphous precipitate. The crystals consist of small hexagonal plates which occur singly and in clusters. The bromide and sulfate ions appear necessary for crystallization.

Terminal prism angles	approx. 57°.
Dichroism	weak, yellow to brown.
Birefringence	weak.
Extinction	parallel.
Limiting concentration	1 mg./ml.
Illustration	figure 81.

(B) H_2PtCl_6 *in 5% HBr.* Crystals similar to the above result.

(C) Na_2PtBr_6. Crystals similar to the above result.

26. K_2PtI_6. An amorphous precipitate forms immediately.

27. Cs_2CdI_4. A colorless precipitate forms immediately.

28. *(A)* CdI_2. A colorless gelatinous precipitate is produced.

(B) $CdBr_2$. A colorless precipitate forms.

(C) $Cd(NO_3)_2 + NH_4SCN$. A turbidity develops.

(D) $CdCl_2$. A slight turbidity forms.

29. *(A)* K_2HgBr_4. A colorless gelatinous precipitate results.

(B) K_2HgBr_4, *acidified.* No change.

30. $K_2Hg(SCN)_4$. A voluminous colorless amorphous precipitate results.

31. *Potassium thallic iodide.* An abundant dark-colored precipitate results.

32. *(A)* H_2SnCl_6. No change.

(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. Long needles are formed, singly, and in sheaves and clusters. This precipitate is composed of the simple quinine sulfate, not a complex thiocyanate. The sulfate is precipitated by reagents containing sulfate ion when they are added to a neutral quinine salt solution.

Birefringence	weak.
Extinction	parallel.
Elongation	positive.

35. $Co(NO_3)_2 + NH_4SCN$. Results similar to those in 34 are obtained.

36. $Cr_2(SO_4)_3 + NH_4SCN$. Results similar to those in 34 are obtained.

37. $NiSO_4 + NH_4SCN$. Results similar to those in 34 are obtained.

38. $Na_3Co(NO_2)_6$. A white amorphous precipitate is formed.

39. *(A)* K_2PdBr_4. An orange-colored amorphous precipitate is formed immediately.

(B) $PdCl_2$ *in HBr.* An orange-colored amorphous precipitate results.

40. Na_2SnI_4. No change.

41. *Diazo reaction.* No change.

Characteristic Test Forms

Quinine is characterized by its tendency to be precipitated from aqueous solution as the sulfate. The quinine sulfate-platino bromide is a useful and unusual test form.

Codeine

The test solution was prepared by dissolving 100 mg. of codeine base, $C_{18}H_{21}O_3N \cdot H_2O$, in distilled water, neutralizing with 0,1 *N* H_2SO_4, and diluting to 10 ml. This gives a solution containing 9,4 mg. of the alkaloid per milliliter. The alkaloid was subjected to the tests of *Amelink*,[12] and found to give the crystals described by this author.

1. *Br_2 in NaBr.* A yellow, amorphous precipitate is formed.

2. *ICl_3.* A copious, white, amorphous precipitate is formed. On standing, dumbbell-like crystals appear, interspersed with some white spherical forms. The test forms are of little value.

Birefringence	weak.
Illustration	figure 6.

3. *(A) $HClO_4$.* No change.
   (B) $NaClO_4$. No change.
4. *$Na_2B_4O_7$.* No change.
5. *NH_4VO_3.* No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* No change.
8. *Sodium veronalate.* No change.
9. *Cupferron.* No marked change occurs; afterev aporation of the solvent, the residue contains oily droplets.
10. *Potassium acid phthalate.* No change.
11. *KBr.* The test drop remains clear at first. On standing, colorless prisms develop singly and in clusters. They are rectangular in form.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Limiting concentration	12 mg./ml.

12. *(A) $SnCl_2$.* On standing, yellow spheres appear, out of which a few long needles grow.
    (B) $SnBr_2$. On standing, yellow spheres appear.
13. *$TiCl_3$.* No change.
14. *$BiCl_3$.* No change.
15. *Potassium antimonyl tartrate.* No change.
16. *$AsCl_3$.* No change.
17. *Mercurochrome.* A copious red precipitate is formed immediately.
18. *$NaAgI_2$.* No change.
19. *(A) $KAuI_2$.* A dark-colored amorphous precipitate forms.
    (B) $HAuI_2$. A dark-colored amorphous precipitate forms.
20. *(A) $NaAuBr_4$.* An orange amorphous precipitate forms immediately.
    (B) $HAuBr_4$. An orange amorphous precipitate forms immediately.

21. $IrCl_4$. No change.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. No change.

25. *(A)* H_2PtCl_6 *in 20% HBr.* An orange precipitate results which changes into oily drops.

(B) H_2PtCl_6 *in 5% HBr.* Results are obtained as in (A).

(C) Na_2PtBr_6. Results are obtained as in (A). Addition of alcohol to the mixture containing the oily drops produces a number or crystalline spheres.

Birefringence	weak. A polarization cross is visible.
Elongation	indeterminate.
Illustration	figure 82.

26. K_2PtI_6. A copious dark-colored precipitate is formed at once.

27. Cs_2CdI_4. At first, no change is observed, but soon a number of small spheres appear, out of which grow transparent rectangular prisms.

Birefringence	strong.
Extinction	oblique.
Elongation	negative.

28. *(A)* CdI_2. Sheaves and clusters of colorless stubby prisms are formed.

Birefringence	weak.
Extinction	oblique, approx. 30° on elongated forms.
Elongation	negative.
Illustration	figure 96.

This is the only CdI_2 derivative obtained having oblique extinction and negative elongation.

(B) $CdBr_2$. No change at first, but on standing, prisms similar to the above result. There is less tendency to form dendrites in this case.

(C) $Cd(NO_3)_2 + NH_4SCN$. The simple codeine thiocyanate is obtained. This consists of long thin needles; some have pointed, others, square ends.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.

(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. An amorphous precipitate is obtained, from which large branching dendritic aggregates of prisms soon grow. Warming promotes crystallization. Single crystals possess pointed ends.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 101.

(B) K_2HgBr_4, *acidified.* Crystals similar to the above are obtained. They are, however, less dendritic in character, *Rosenthaler*[24] describes the form of this precipitate.

30. $K_2Hg(SCN)_4$. A copious, oily, colorless precipitate forms at once.

31. *Potassium thallic iodide.* A heavy, dark-colored precipitate is obtained.

32. *(A)* H_2SnCl_6. No change.
(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 - NH_4SCN$. The simple codeine thiocyanate forms as in 28 (C).

35. $Co(NO_3)_2 + NH_4SCN$. Blue oily drops form.

36. $Cr_2(SO_4)_3 - NH_4SCN$. The simple codeine thiocyanate is obtained as in 28 (C).

37. $NiSO_4 - NH_4SCN$. The simple codeine thiocyanate is obtained as in 28 (C).

38. $Na_3Co(NO_2)_6$. No change.

41. *Diazo reaction.* A colorless precipitate appears.

Characteristic Test Forms

The most characteristic reaction is obtained in the cadmium iodide test. Likewise, potassium mercuric bromide appears useful since relatively few alkaloids give crystalline precipitates with the neutral potassium mercuric bromide reagent.

Dionine

The test solution was prepared by dissolving 105 mg. of dionine, the hydrochloride of ethyl morphine, in 10 ml. of distilled water. This gives a solution containing 10 mg. of $C_{19}H_{23}O_3N \cdot HCl$ per milliliter. The alkaloid was found to meet the standards of purity of the U. S. Pharmacopeia X.

1. Br_2 *in* $NaBr$. A yellow amorphous precipitate forms.
2. ICl_3. A yellow precipitate forms at once.
3. *(A)* $HClO_4$. No change.
(B) $NaClO_4$. No change.
4. $Na_2B_4O_7$. No change.
5. NH_4VO_3. No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* No change.
8. *Sodium veronalate.* No change.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.

11. *KBr.* No change.
12. $SnCl_2$. No change.
13. $TiCl_3$. No change.
14. $BiCl_3$. No change.
15. *Potassium antimonyl tartrate.* No change.
16. $AsCl_3$. No change.
17. *Mercurochrome.* A copious red precipitate is formed immediately.
18. $NaAgI_2$. No change.
19. *(A)* $KAuI_2$. A dark-colored precipitate forms at once.
    (B) $HAuI_2$. A dark-colored precipitate forms at once.
20. *(A)* $NaAuBr_4$. A red-colored amorphous precipitate is formed.
    (B) $HAuBr_4$. A red-colored amorphous precipitate is formed.
21. $IrCl_4$. A slight, light-brown precipitate is obtained.
22. $RhCl_3$. No change.
23. $RuCl_3$. No change.
24. Na_2OsCl_6. No change.
25. *(A)* H_2PtCl_6 *in 20% HBr.* An amorphous precipitate separates, from which, on standing and upon scratching the slide, large irregular rosettes of pointed prisms crystallize.

Dichroism	orange to yellow.
Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Limiting concentration	5 mg./ml.
Illustration	figure 83.

(B) H_2PtCl_6 *in 5% HBr.* Crystals are formed similar to the above. The individual prisms are somewhat broader and the rosettes more symmetrical. Large prisms with notched ends may be noted occasionally.

Limiting concentration	3 mg./ml.

(C) Na_2PtBr_6. Crystals practically identical with those in (B) are formed. The bromplatinate crystals can be recrystallized from alcohol, whereby somewhat smaller and thinner hexagonal prisms result. *Amelink*[12] and *Stephenson*[11] describe the chlorplatinate of this alkaloid as amorphous.

26. K_2PtI_6. A copious, dark-colored precipitate is formed at once.
27. Cs_2CdI_4. No change.
28. *(A)* CdI_2. No change.
    (B) $CdBr_2$. No change.
    (C) $Cd(NO_3)_2 + NH_4SCN$. A few oily drops form on standing.
    (D) $CdCl_2$. No change.
29. *(A)* K_2HgBr_4. A white precipitate is formed immediately but no crystals separate.

(B) K_2HgBr_4, *acidified.* An amorphous precipitate is formed. On warming, with stirring, quite a few needles and pointed prisms are formed,

some collecting into groups of three and more. Occasionally oblong plates may be noted. These crystals cannot readily be distinguished from those obtained with codeine and K_2HgBr_4.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Illustration	figure 107.

30. $K_2Hg(SCN)_4$. A turbidity is produced.

31. *Potassium thallic iodide.* A copious, red precipitate forms at once.

32. *(A)* H_2SnCl_6. No change.
(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 - NH_4SCN$. A few crystals of the simple alkaloid thiocyanate are formed.

35. $Co(NO_3)_2 + NH_4SCN$. A blue turbidity forms.

36. $Cr_2(SO_4)_3 - NH_4SCN$. On standing, a large number of crystals of the alkaloid thiocyanate are obtained.

37. $NiSO_4 - NH_4SCN$. A number of crystals of the simple alkaloid thiocyanate are obtained. For purposes of comparison with complex metallo-thiocyanates obtained with other alkaloids, the properties of the simple dionine thiocyanate, as obtained by adding a few crystals of NH_4SCN to a drop of the 1% dionine test solution, are tabulated. The crystals consist of long pointed prisms occurring singly and in groups.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.

38. $Na_3Co(NO_2)_6$. A turbidity appears on standing for a few minutes.

39. *(A)* K_2PdBr_4. An orange precipitate forms.
(B) $PdCl_2$ *in* HBr. An orange precipitate forms.

40. Na_2SnI_4. A precipitate forms which, on warming, yields a few spherical clusters of crystals. These polarize brightly, but irregularly.

Illustration	figure 135.

41. *Diazo reaction.* No change.

Characteristic Test Forms

The most useful test for the identification of dionine is the precipitation of the bromplatinate. The crystals are easily obtained and possess characteristic forms.

Heroine

The test solution was prepared by dissolving 120 mg. of heroine hydrochloride monohydrate in 10 ml. of distilled water. This gives a

solution containing 10 mg. of the alkaloid per milliliter. The alkaloid was subjected to the tests of *Amelink*[12] and gave exactly the same crystals as described by this author.

1. *Br_2 in NaBr.* A yellow amorphous precipitate forms.
2. *ICl_3.* A yellow amorphous precipitate forms.
3. *(A) $HClO_4$.* No change.
   (B) $NaClO_4$. No change.
4. *$Na_2B_4O_7$.* On standing, a few droplets of oil appear around the edge of the test drop.
5. *NH_4VO_3.* No change.
6. *Potassium anthraquinone sulfonate.* After standing a few minutes, many clumps and sheaves of dark-yellow needles are formed.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 25.

7. *Potassium xanthate.* A turbidity forms.
8. *Sodium veronalate.* No change.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.
11. *KBr.* No change.
12. *(A) $SnCl_2$.* No change.
    (B) $SnBr_2$. No change.
13. *$TiCl_3$.* No change.
14. *$BiCl_3$.* No change.
15. *Potassium antimonyl tartrate.* No change.
16. *$AsCl_3$.* No change.
17. *Mercurochrome.* A red precipitate forms immediately.
18. *$NaAgI_2$.* No change.
19. *(A) $KAuI_2$.* A copious, black, amorphous precipitate is obtained.
    (B) $HAuI_2$. Results are obtained as in (A).
20. *(A) $NaAuBr_4$.* A orange-colored amorphous precipitate results at once.
    (B) $HAuBr_4$. Results are obtained as in (A).
21. *$IrCl_4$.* A brown precipitate is formed immediately. On standing three or four minutes, a number of reddish-brown spheres appear.

Birefringence	weak.
Other optical data	difficult to obtain.
Illustration	figure 64.

22. *$RhCl_3$.* No change.
23. *$RuCl_3$.* No change.
24. *Na_2OsCl_6.* No change.

25. *(A)* H_2PtCl_6 *in 20% HBr.* A copious orange precipitate results at once.

(B) H_2PtCl_6 *in 5% HBr.* Small spherulites of rectangular prisms are obtained on standing some time, or on warming the initial amorphous precipitate.

Dichroism	yellow to brown.
Birefringence	weak.
Extinction	parallel.
Elongation	negative; in no other case does this reagent give crystals that have the just-mentioned extinction and elongation.
Limiting concentration	3 mg./ml.
Illustration	figure 84.

(C) Na_2PtBr_6. Results are obtained as in (B). Crystals appear larger, however.

26. K_2PtI_6. A dark precipitate appears immediately.

27. Cs_2CdI_4. A rather slight precipitate forms, from which there develop a large number of small irregular transparent spheres.

Birefringence	very weak.

28. *(A)* CdI_2. An amorphous precipitate is formed.

(B) $CdBr_2$. An amorphous precipitate is formed.

(C) $Cd(NO_3)_2 + NH_4SCN$. Oily droplets form on standing.

(D) $CdCl_2$. On standing, there appear along the edge of the test drop, a number of large, well-formed rectangular plates. Some form in overlapping groups.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 93.

29. *(A)* K_2HgBr_4. A white precipitate forms immediately.

(B) K_2HgBr_4, *acidified.* Results are obtained as in (A).

30. $K_2Hg(SCN)_4$. A copious colorless precipitate results at once.

31. *Potassium thallic iodide.* A dark-orange precipitate forms.

32. *(A)* H_2SnCl_6. No change.

(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. No change.

35. $Co(NO_3)_2 + NH_4SCN$. On standing, a slight, blue turbidity forms.

36. $Cr_2(SO_4)_3 + NH_4SCN$. No change.

37. $NiSO_4 + NH_4SCN$. No change.

38. $Na_3Co(NO_2)_6$. A yellow turbidity is produced at once.

39. *(A)* K_2PdBr_4. An orange precipitate forms.
(B) $PdCl_2$ *in HBr.* Results are obtained as in (A).

40. Na_2SnI_4. Simple, yellow sphere-like crystals form from the amorphous precipitate. Occasionally these collect into aggregates.

Birefringence	weak.
Other optical data	difficult to obtain.
Illustration	figure 173.

41. *Diazo reaction.* No change.

Characteristic Test Forms

The most specific test is that obtained with $CdCl_2$. None of the other alkaloids studied give crystals with this reagent. The heroine precipitate is, however, relatively soluble. The crystals obtained with the Na_2PtBr_6 reagent are characteristic when their optical properties are considered. The test with anthraquinone sulfonate is of some use because of the few alkaloids producing crystalline precipitates with this reagent.

Morphine

The test solution was prepared by dissolving 0,143 g. of morphine hydrochloride, $C_{17}H_{19}O_3N \cdot HCl \cdot 3\,H_2O$, in 10 ml. of distilled water. This gives a solution containing 10 mg. of the alkaloid per milliliter. The solution was found to give the tests described by *Amelink*[12] for morphine.

1. Br_2 *in* $NaBr$. A slight yellow precipitate forms which redissolves on standing.

2. ICl_3. A few, irregularly formed, small clusters of crystals result.

Birefringence	weak. The crystals are too poorly formed for other optical observations.
Illustration	figure 7.

3. *(A)* $HClO_4$. A rather slight precipitate forms which is composed of colorless thin needles.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	5 mg./ml.

(B) $NaClO_4$. Crystals are obtained as in (A) but in larger quantity. Optical properties are the same as described in (A).

4. $Na_2B_4O_7$. No change.

5. NH_4VO_3. No change.

6. *Potassium anthraquinone sulfonate.* No change.

7. *Potassium xanthate.* No change.

8. *Sodium veronalate.* No change.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.
11. *KBr.* No change.
12. *(A)* $SnCl_2$. No change.
    (B) $SnBr_2$. No change.
13. $TiCl_3$. No change.
14. $BiCl_3$. No change.
15. *Potassium antimonyl tartrate.* No change.
16. $AsCl_3$. No change.
17. *Mercurochrome.* A bulky, red precipitate results immediately.
18. $NaAgI_2$. No change.
19. *(A)* $KAuI_2$. A dark-colored precipitate is formed. On standing some time, a number of dark-brown clusters of overlapping plates are often obtained. These crystals are formed by the action of the free iodine in the reagent, and are the same as those obtained with *Wagner's* reagent (I_2 in KI).

Dichroism	red to brown.
Birefringence	weak.
Extinction	parallel.
Elongation	negative.

(B) $HAuI_2$. A dark-colored precipitate is formed. Occasionally crystals develop as in (A).

20. *(A)* $NaAuBr_4$. An orange-colored precipitate forms at once.
    (B) $HAuBr_4$. An orange-colored precipitate forms at once.
21. $IrCl_4$. No change.
22. $RhCl_3$. No change.
23. $RuCl_3$. No change.
24. Na_2OsCl_6. No change.
25. *(A)* H_2PtCl_6 *in 20%* HBr. No change.
    (B) H_2PtCl_6 *in 5%* HBr. No change.
    (C) Na_2PtBr_6. No change.
26. K_2PtI_6. A copious, black precipitate is formed immediately.
27. Cs_2CdI_4. No change.
28. *(A)* CdI_2. A large number of clusters of fine needles form immediately.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 95.

(B) $CdBr_2$. No change.
(C) $Cd(NO_3)_2 + NH_4SCN$. No change.
(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. A large number of very light-colored thin clusters of needles appear at once. The form of this precipitate is described by *Behrens*.[25]

Birefringence	weak.
Other optical properties	difficult to establish.
Limiting concentration	1 mg./ml.
Illustration	figure 102.

(B) K_2HgBr_4, *acidified.* No change.

30. $K_2Hg(SCN)_4$. No change. Morphine, caffeine, and theobromine are the only alkaloids studied that give no precipitate with this reagent.

31. *Potassium thallic iodide.* An orange precipitate forms immediately.

32. *(A)* H_2SnCl_6. No change.

(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. No change.

35. $Co(NO_3)_2 + NH_4SCN$. No change.

36. $Cr_2(SO_4)_3 + NH_4SCN$. No change.

37. $NiSO_4 + NH_4SCN$. No change.

38. $Na_3Co(NO_2)_6$. No change.

39. *(A)* K_2PdBr_4. No change.

(B) $PdCl_2$ *in* HBr. No change.

40. Na_2SnI_4. Yellow, flower-like aggregates, composed of rounded clusters, form very soon from the initial precipitate.

Birefringence	weak.
Other optical properties	difficult to establish.
Limiting concentration	2 mg./ml.
Illustration	figure 137.

41. *Diazo reaction.* A faintly pink oil is formed. This color cannot be confused with that given in the novocaine diazonium test.

Characteristic Test Forms

The sodium tin iodide derivative is characteristic in appearance; codeine and dionine, however, give the same type of crystals, although not as easily. The potassium mercuric bromide precipitate is characteristic since this reagent yields crystalline precipitates with relatively few alkaloids and in no other case does the precipitate have this particular appearance.

Narcotine

The test solution was prepared by dissolving 100 mg. of the anhydrous base in 0,1 N HCl and diluting with water to 10 ml. This gives a solution containing 10 mg. of the base per milliliter. The solution was found to give exactly the same crystals as *Amelink*[12] describes for narcotine.

1. *Br_2 in $NaBr$.* A yellow amorphous precipitate forms immediately.
2. *ICl_3.* A slight cream-colored precipitate is formed at once.
3. *(A) $HClO_4$.* A turbidity is produced immediately.
   (B) $NaClO_4$. A turbidity is produced immediately.
4. *$Na_2B_4O_7$.* A white precipitate is formed at once. It soon crystallizes into symmetrical aggregates of needles. On warming the test drop, the precipitate dissolves due to rupture of the lactone ring and formation of the sodium salt. Needles are again obtained on cooling.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Limiting concentration	0,3 mg./ml.
Illustration	figure 21.

5. *NH_4VO_3.* A copious yellow precipitate results.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* A turbidity forms.
8. *Sodium veronalate.* A turbidity forms.
9. *Cupferron.* A turbidity forms.
10. *Potassium acid phthalate.* No change.
11. *KBr.* No change.
12. *$SnCl_2$.* A turbidity forms.
13. *$TiCl_3$.* A turbidity forms.
14. *$BiCl_3$.* No change.
15. *Potassium antimonyl tartrate.* No change.
16. *$AsCl_3$.* No change.
17. *Mercurochrome.* A copious red precipitate is formed immediately.
18. *$NaAgI_2$.* No change.
19. *(A) $KAuI_2$.* A dark-colored precipitate is formed at once.
    (B) $HAuI_2$. A dark-colored precipitate is formed at once.
20. *(A) $NaAuBr_4$.* A brownish-colored precipitate forms at once.
    (B) $HAuBr_4$. A brownish-colored precipitate forms at once.
21. *$IrCl_4$.* A brown-colored amorphous precipitate is formed at first; on standing, quite a few fine bundles of needles appear.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 65.

22. *$RhCl_3$.* A slight amorphous precipitate forms.
23. *$RuCl_3$.* A slight amorphous precipitate forms.
24. *Na_2OsCl_6.* A copious yellow precipitate results immediately.
25. *(A) H_2PtCl_6 in 20% HBr.* A red-colored amorphous precipitate is produced at once.
    (B) H_2PtCl_6 in 5% HBr. Results are obtained as in (A).
    (C) Na_2PtBr_6. Results are obtained as in (A).

26. K_2PtI_6. A dark-colored amorphous precipitate is produced.
27. Cs_2CdI_4. A copious white precipitate forms at once.
28. *(A)* CdI_2. A copious white precipitate forms at once.
    (B) $CdBr_2$. A white precipitate is produced.
    (C) $Cd(NO_3)_2 + NH_4SCN$. A colorless precipitate is formed.
    (D) $CdCl_2$. No change.
29. *(A)* K_2HgBr_4. A colorless non-crystalline precipitate results.
    (B) K_2HgBr_4, *acidified*. Results are as in (A).
30. $K_2Hg(SCN)_4$. A copious colorless precipitate forms immediately.
31. *Potassium thallic iodide*. A copious dark-precipitate appears.
32. *(A)* H_2SnCl_6. No change.
    (B) $H_2SnCl_6 + KBr$. No change.
33. $HSbCl_4$. No change.
34. $MnSO_4 + NH_4SCN$. A turbidity is produced.
35. $Co(NO_3)_2 + NH_4SCN$. A blue turbidity is produced.
36. $Cr_2(SO_4)_3 + NH_4SCN$. A turbidity is produced.
37. $NiSO_4 + NH_4SCN$. A turbidity is produced.
38. $Na_3Co(NO_2)_6$. A voluminous orange precipitate appears.
39. *(A)* K_2PdBr_4. A copious brown precipitate appears at once.
    (B) $PdCl_2$ *in HBr*. Results are obtained as in (A).
40. Na_2SnI_4. No change.
41. *Diazo reaction*. A yellow coloration is obtained.

Characteristic Test Forms

This alkaloid is characterized by the fact that it gives precipitates with a large number of reagents. Most of the precipitates formed are non-crystalline. The most characteristic test is that with sodium tetraborate if the optical properties of the crystals and the solubility of the precipitate in the hot reagent are considered. The crystalline test forms produced by $IrCl_4$ are specific but not as easily obtained as the ones with borax.

Papaverine

The test solution was prepared by dissolving 100 mg. of the anhydrous alkaloid in 0,1 *N* HCl and diluting the resulting solution with water to 10 ml. This gave a solution containing 10 mg. of the base per milliliter. The tests for papaverine described by *Amelink*[12] were obtained on this solution.

1. Br_2 *in NaBr*. A yellow amorphous precipitate forms immediately.
2. ICl_3. A colorless amorphous precipitate forms.
3. *(A)* $HClO_4$. A colorless precipitate forms which redissolves on standing.
   (B) $NaClO_4$. Results are obtained as in (A).

4. $Na_2B_4O_7$. The free base precipitates in an oily form; addition of a drop of alcohol produces an excellent crystallization. The crystals are small prisms with slanting or notched ends. They often combine to form spherulites.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Limiting concentration	1 mg./ml., *Amelink*.[12]
Illustration	figure 22.

5. NH_4VO_3. A yellow non-crystalline precipitate forms.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* A turbidity forms.
8. *Sodium veronalate.* A turbidity forms.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.
11. KBr. No change.
12. *(A)* $SnCl_2$. A colorless amorphous precipitate forms.
(B) $SnCl_2 + KBr$. Results are obtained as in (A).
13. $TiCl_3$. A precipitate is formed which soon crystallizes into elongated hexagonal plates, arranging themselves into somewhat symmetrical clusters.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	2 mg./ml.
Illustration	figure 40.

14. $BiCl_3$. No change.
15. *Potassium antimonyl tartrate.* No change.
16. $AsCl_3$. No change.
17. *Mercurochrome.* A red-colored amorphous precipitate is formed.
18. $NaAgI_2$. No change.
19. *(A)* $KAuI_2$. A copious dark-colored precipitate is produced.
(B) $HAuI_2$. A copious dark-colored precipitate is produced.
20. *(A)* $NaAuBr_4$. A copious orange precipitate is produced.
(B) $HAuBr_4$. A copious orange precipitate is produced.
21. $IrCl_4$. A copious brown precipitate results.
22. $RhCl_3$. A copious dark-colored precipitate forms.
23. $RuCl_3$. No change.
24. Na_2OsCl_6. A yellow amorphous precipitate results.
25. *(A)* H_2PtCl_6 *in 20% HBr.* A copious orange precipitate is formed at first. On warming and scratching the slide, a few red diamond-shaped crystals appear. These are the only crystals of this shape obtained with this reagent.

Birefringence	strong.
Extinction	parallel.
Elongation	indefinite.
Illustration	figure 85.

(B) H_2PtCl_6 *in 5% HBr.* Results are obtained as in (A), but more crystals are formed.

(C) Na_2PtBr_6. A few crystals of the type described in (A) are obtained.

26. K_2PtI_6. A copious brownish-red precipitate results at once.

27. Cs_2CdI_4. An amorphous precipitate is formed from which many thin transparent rectangular plates are soon obtained. These collect into groups somewhat irregular in form, with the individual plates pointing outward in different planes.

Birefringence	weak.
Extinction	parallel.
Elongation	positive.

28. *(A)* CdI_2. Crystals are obtained with the form and properties of those in 27. The crystals are obtained somewhat more readily than with the Cs_2CdI_4 reagent.

Limiting concentration	1 mg./ml.
Illustration	figure 97.

(B) $CdBr_2$. No change at first; on standing, a few rectangular prisms are obtained.

(C) $Cd(NO_3)_2 + NH_4SCN$. A turbidity is produced.

(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. An amorphous precipitate forms immediately.

(B) $HgCl_2$ *in HBr.* An amorphous precipitate forms immediately.

30. $K_2Hg(SCN)_4$. A dense turbidity forms.

31. *Potassium thallic iodide.* A dark-colored precipitate is produced.

32. *(A)* H_2SnCl_6. A white amorphous precipitate is obtained.

(B) $H_2SnCl_6 + KBr$. A white amorphous precipitate is obtained.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. An oil is formed.

35. $Co(NO_3)_2 + NH_4SCN$. A blue turbidity results.

36. $Cr_2(SO_4)_3 + NH_4SCN$. An oil results, from which, on standing, small transparent plates appear. These crystals are the simple papaverine thiocyanate.

Birefringence	weak.
Extinction	oblique.
Elongation	negative.

37. $NiSO_4 + NH_4SCN$. An amorphous precipitate is obtained.

38. $Na_3Co(NO_2)_6$. A copious precipitate forms.

39. *(A)* K_2PdBr_4. A brown amorphous precipitate results at once.
(B) $PdCl_2$ *in* HBr. A brown amorphous precipitate results at once.

40. Na_2SnI_4. No change.

41. *Diazo reaction.* No change.

Characteristic Test Forms

Papaverine gives a large number of precipitates as outlined above; in fact, almost two-thirds of the reagents studied produce precipitation. Unfortunately, few of this number develop into useful crystalline forms. The cadmium iodide derivative yields a specific test. The titanium salt is also characteristic.

Brucine

The test solution was prepared by dissolving 109 mg. of brucine, $C_{23}H_{26}N_2O_4 \cdot 2\,H_2O$, in 0,1 *N* HCl and diluting with water to 10 ml. This gave a solution containing 10 mg. of the base per milliliter. The solution was subjected to the tests of *Amelink*[12] and gave the crystals described by this author.

1. Br_2 *in* $NaBr$. A slight yellow-colored precipitate forms upon scratching. It consists of tiny, dark crystalline aggregates which polarize irregularly and have little value for identification purposes.

Illustration ..... figure 4.

2. ICl_3. A yellow amorphous precipitate develops immediately.

3. *(A)* $HClO_4$. The solution, remains clear, at first, but on standing and scratching, a number of large, well-formed rhombs crystallize. Some of these form into spherulites.

Principal angle	approx. 108°.
Birefringence	strong.
Extinction	symmetrical.
Elongation	not definite.
Limiting concentration	10 mg./ml.
Illustration	figure 11.

(B) $NaClO_4$. Crystals similar to those in (A) are obtained. Spherulites are more common in this case.

4. $Na_2B_4O_7$. The free base precipitates in groups of fine needles.

Birefringence	strong; a polarization cross is obtained.
Extinction	parallel and oblique.
Elongation	negative.
Illustration	figure 23.

5. NH_4VO_3. A copious yellow precipitate forms at once.

6. *Potassium anthraquinone sulfonate.* No change.

7. *Potassium xanthate.* On standing, or more rapidly upon scratching the slide, there are produced, even from slightly acid solution, a large number of oblong plates. Some of them collect into clusters. The crystals obtained with isopropyl xanthate are similar but somewhat larger and better formed. The properties for the ethyl xanthate are tabulated below.

Birefringence	strong.
Extinction	chiefly parallel, occasionally oblique views.
Elongation	not definite.
Illustration	figure 38.

8. *Sodium veronalate.* Slanting and clipped-ended prisms are obtained. These are probably a form of the free alkaloid base.

Birefringence	strong.
Extinction	parallel and oblique.
Elongation	negative.

9. *Cupferron.* No change.

10. *Potassium acid phthalate.* No change.

11. *KBr.* No change.

12. *(A) $SnCl_2$.* From the clear solution there soon appear a few rather thick needles which arrange themselves into groups.

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Illustration	figure 35.

13. *$TiCl_3$.* On standing a short while, colorless, ragged, pointed prisms of low refractive index are obtained from the clear solution. They occur singly or in small clusters. On longer standing, these crystals dissolve. Better crystals are obtained by now adding more water which again causes precipitation.

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Limiting concentration	5 mg./ml.
Illustration	figure 42.

14. *$BiCl_3$.* On standing, large yellow tufts of fine needles appear. This is a very specific test for the identification of brucine.

Birefringence	weak; a polarization cross appears.
Extinction	parallel.
Elongation	positive.
Limiting concentration	5 mg./ml.
Illustration	figure 43.

15. *Potassium antimonyl tartrate.* No change.

16. *$AsCl_3$.* No change.

17. *Mercurochrome.* A copious red precipitate is formed immediately.

18. $NaAgI_2$. Crystals are formed almost at once. The six-sided plates often form clusters, and probably consist of the simple brucine hydriodide.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.

19. *(A)* $KAuI_2$. A black amorphous precipitate forms at once.
(B) $HAuI_2$. A black amorphous precipitate forms at once.

20. *(A)* $NaAuBr_4$. A brown amorphous precipitate forms.
(B) $HAuBr_4$. A brown amorphous precipitate forms.

21. $IrCl_4$. A yellow amorphous precipitate is produced, from which, almost immediately, appear irregularly branching needles which often collect into clumps.[26]

Birefringence	weak.
Extinction	parallel.
Elongation	positive.
Illustration	figure 67.

22. $RhCl_3$. On standing, a number of colorless, irregularly formed needles appear. They occur singly and in pairs.[26]

Birefringence	weak.
Extinction	parallel.
Elongation	positive.
Limiting concentration	10 mg./ml.
Illustration	figure 118.

23. $RuCl_3$. A dark-colored amorphous precipitate forms, from which long needles appear on standing.[26]

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Limiting concentration	5 mg./ml.
Illustration	figure 121.

24. Na_2OsCl_6. A precipitate of finely pointed prisms, singly and in sheaves, separates immediately. The crystalline appearance, but not the optical character of the crystals from these four platinum group metals (21, 22, 23, 24), has been described by *Whitmore* and *Schneider*.[26]

Birefringence	weak.
Extinction	parallel.
Elongation	positive.
Limiting concentration	1 mg./ml.
Illustration	figure 73.

[26] *W. F. Whitmore* and *H. Schneider,* Mikrochemie **17**, 279 (1935).

25. *(A)* H_2PtCl_6 *in 20% HBr.* A copious yellow precipitate appears, which changes shortly into long needle-like forms. These are similar to the brucine platino chloride crystals but somewhat smaller.

Birefringence	weak.
Extinction	parallel.
Elongation	positive.
Illustration	figure 86.

(B) H_2PtCl_6 *in 5% HBr* and *(C)* Na_2PtBr_6. Results are obtained as in (A).

26. K_2PtI_6. A dark-colored amorphous precipitate is obtained.

27. Cs_2CdI_4. An amorphous precipitate is formed, and from this oily droplets separate which change into yellow spheres. These grow into aggregates of pointed prisms.

Birefringence	weak, the smaller crystals give a polarization cross.
Extinction	oblique on prisms.
Elongation	positive.

28. *(A)* CdI_2. Results are the same as with 27.

Illustration	figure 98.

(B) $CdBr_2$. From the initial amorphous precipitate, a number of somewhat irregular clusters of slant-ended prismatic forms are soon obtained. Their form is similar to the larger prisms obtained with CdI_2.

Birefringence	strong.
Extinction	oblique.
Elongation	positive.

(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. An amorphous precipitate is formed immediately, from which, on standing, a number of fine mossy aggregates of dendritic needles develop. The ends of the needles broaden out into prismatic shape. *Rosenthaler*[24] describes the form of this precipitate.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 103.

(B) K_2HgBr_4, *acidified.* Results similar to those in (A) are obtained. The clusters, however, tend to develop into more prismatic forms.

30. $K_2Hg(SCN)_4$. An amorphous precipitate is produced from which there soon develop large colorless dendritic aggregates of needles and small spherulites.

Birefringence	weak; the spherulites yield a polarization cross.
Extinction	indefinite.
Elongation	negative.
Illustration	figure 103.

31. *Potassium thallic iodide.* A voluminous red precipitate is obtained at once.

32. *(A)* H_2SnCl_6. From the clear solution, on standing, numbers of colorless pointed prisms appear, a few of them collecting into clusters.

Birefringence	weak.
Extinction	parallel.
Elongation	positive.
Illustration	figure 113.

(B) $H_2SnCl_6 + KBr$. There are formed immediately many, rather small, pointed prisms which often collect into aggregates. Optical constants are as obtained in (A).

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. Brilliantly anisotropic aggregates of hexagonal plates are formed.

Birefringence	very strong.
Extinction	parallel (or symmetrical).
Elongation	indefinite.
Illustration	figure 116.

35. $Co(NO_3)_2 + NH_4SCN$. On standing, many dark-blue spheres are formed; they are composed of fine needles.

Birefringence	weak; a polarization cross is obtained.
Extinction	indefinite.
Elongation	positive.
Illustration	figure 123.

Behrens-Kley[25] describes a brucine cobalti thiocyanate, but of a somewhat different crystalline form.

36. $Cr_2(SO_4)_3 + NH_4SCN$. Groups of ragged prisms occasionally appear, which cannot readily be distinguished from the simple brucine thiocyanate.

37. $Na_3Co(NO_2)_6$. A copious, oily precipitate is formed, from which, clusters of very weakly birefringent needles separate. Optical data are not obtainable.

38. $NiSO_4 + NH_4SCN$. Thin, blue, pointed plates appear. They are arranged in groups of somewhat irregular character.

Birefringence	strong.
Extinction	parallel and symmetrical.
Elongation	not definite.
Illustration	figure 125.

39. *(A)* K_2PdBr_4. A yellow amorphous precipitate is obtained which almost immediately gives aggregates of fine needles. Some coarser groups appear, made of thin pointed plates.

Birefringence	weak; a polarization cross is obtained.
Extinction	parallel, obtained on plates.
Elongation	positive.
Limiting concentration	2 mg./ml.
Illustration	figure 128.

(B) $PdCl_2$ in HBr. Many aggregates of the thin pointed plates described under (A) are formed. Optical properties are the same as in (A).

40. *Na_2SnI_4.* A precipitate is formed, from which there develop a number of small aggregates of irregular plates of low refractive index. They are difficult to observe unless polarized light is employed. The crystals are too irregular for ready determination of optical constants.

Birefringence	weak.
Illustration	figure 139.

41. *Diazo reaction.* No change.

Characteristic Test Forms

Brucine is characterized by the very large number of crystalline derivatives it is capable of producing. The alkaloid is second only to strychnine in this respect. Therefore it is difficult to name the most useful test. One may list first, the crystals produced with $BiCl_3$. Although strychnine too yields crystals with this reagent, they are different in shape and in sign of elongation. Thus, employing the sign of elongation, $BiCl_3$ provides an especially characteristic test for brucine. None of the other nineteen alkaloids yield crystals with this reagent. Rhodium-chloride, also gives crystals only with strychnine. Ruthenium gives crystals with strychnine and cocaine in addition to brucine. The potassium mercury thiocyanate and the potassium xanthate precipitates are quite characteristic.

Strychnine

The test solution was prepared by dissolving 128 mg. of strychnine sulfate, $(C_{21}H_{22}O_2N_2)_2 \cdot H_2SO_4 \cdot 5\ H_2O$, in 10 ml. of distilled water. This gives a solution containing 10 mg. of the alkaloid per milliliter. The alkaloid was found to meet the tests for purity of the United States Pharmacopeia X.

1. *Br_2 in NaBr.* A yellow turbidity was produced at once.

2. *ICl_3.* A white precipitate is formed in which small transparent spheres appear. These grow into star-like and dendritic aggregates of prismatic forms.

Illustration	figure 8.

3. *(A)* $HClO_4$. A crystalline precipitate is formed composed of transparent lath-like prisms Their refractive index is so low that they are more easily observed under crossed nicols. Occasionally small prisms may be noted mixed with the larger forms. This test is described by *Chamot* and *Mason*[17] as a reaction for the perchlorate ion. Strychnine is the only alkaloid studied giving crystals of this form with $HClO_4$.

Birefringence	weak.
Extinction	parallel on elongated prisms; oblique on small rectangles (see *Poe* and *Sellers*[27]).
Elongation	negative.
Limiting concentration	1 mg./ml.
Illustration	figure 12.

(B) $NaClO_4$. Crystals are obtained similar to the above; there is, however, a greater tendency toward formation of clusters.

4. $Na_2B_4O_7$. The free base is immediately precipitated in the form of long tetragonal prisms.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Illustration	figure 24.

5. NH_4VO_3. A yellow precipitate is formed, from which appear many long thin needles and occasional clusters. Some of these grow into wider prismatic forms.

Birefringence	very weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	2 mg./ml.
Illustration	figure 6.

6. *Potassium anthraquinone sulfonate.* Sheaves and clusters of yellow needles are formed. The individual forms are very fine.

Birefringence	very weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 29.

7. *Potassium xanthate.* A precipitate is formed immediately, made up of tablets, singly, and in clusters. The isopropyl xanthate derivative is more elongated than the simpler xanthate. These crystalline xanthates are soluble in acetic acid.

Birefringence	strong.
Extinction	parallel and symmetrical.

[27] *C. F. Poe* and *T. E. Sellers*, J. Amer. Chem. Soc. **54**, 249 (1932).

Elongation	indefinite.
Illustration	figure 37.

8. *Sodium veronalate.* Needles similar to those of the free alkaloid base are formed.

9. *Cupferron.* A slight amount of colorless oil is produced.

10. *Potassium acid phthalate.* A number of well-formed pyramidal prisms are soon obtained. These, on standing, develop to a good size. The pyramidal structure is best observed under crossed nicols.

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Limiting concentration	0,5 mg./ml.
Illustration	figure 39.

11. *KBr.* No change.

12. *(A) $SnCl_2$.* Dendritic aggregates and clusters composed of stubby prisms are produced.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	2 mg./ml.
Illustration	figure 36.

(B) $SnBr_2$. Results are obtained similar to the ones with $SnCl_2$. The crystals are smaller and the test more sensitive.

13. *$TiCl_3$.* A precipitate is formed at once. It is composed of large needles in aggregates. The form of these crystals is distinct from the others obtained with this reagent.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Limiting concentration	2 mg./ml.
Illustration	figure 41.

14. *$BiCl_3$.* First, an amorphous precipitate is produced. Soon after there are formed a large number of stubby prisms, collecting in compact radiating aggregates. The sign of elongation distinguishes this test from the test with brucine and $BiCl_3$.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 44.

15. *Potassium antimonyl tartrate.* On stirring the test drop, a precipitate of isotropic square crystalline forms is obtained. The crystals thus belong to the regular system. They are the only ones of this type obtained in this study. On standing, the crystals grow and become

pyramidal. Qualitative tests on this precipitate indicate that it is not a simple tartrate but contains antimony.

Birefringence	none.
Illustration	figure 45.

16. $AsCl_3$. No change.

17. *Mercurochrome*. A red amorphous precipitate is formed. A few, irregularly shaped aggregates are produced on warming the precipitated mass. These are not definitely anisotropic.

18. $NaAgI_2$. Crystals form similar to the simple strychnine iodide. The iodide consists of long needles and prisms, often collecting into groups. They have a high refractive index.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.

19. *(A)* $KAuI_2$. An abundant dark precipitate is obtained. This is composed of small dark-colored needles.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 49.

(B) $HAuI_2$. Results are the same as in (A).

20. *(A)* $NaAuBr_4$. An orange-colored amorphous precipitate results.

(B) $HAuBr_4$. Results are obtained as in (A).

21. $IrCl_4$. First, a brown flocculent precipitate is produced, from which one gets symmetrical aggregates composed of small brown needles and tiny rectangular prisms.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	2 mg./ml.
Illustration	figure 68.

22. $RhCl_3$. A dark-colored amorphous precipitate is formed. On standing, spherulites of dark needles are obtained.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 119.

23. $RuCl_3$. On standing, groups of very small, radiating, rectangular prisms are observed.

Dichroism	brown to yellow-brown.
Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 122.

24. Na_2OsCl_6. A yellow precipitate is produced at once. It is composed of rectangular prisms and pyramids. Some of them collect into radiating groups.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Illustration	figure 74.

25. *(A)* H_2PtCl_6 *in 20% HBr.* An orange-colored precipitate is formed, from which appear numbers of fine needles collecting into clusters. On standing, some of these needles form small prisms.

Birefringence	strong; a polarization cross is obtained under crossed nicols.
Extinction	parallel.
Elongation	positive.
Limiting concentration	0,2 mg./ml.
Illustration	figure 68.

(B) H_2PtCl_6 *in 5% HBr.* The precipitate and crystals are the same as in (A).

(C) Na_2PtBr_6. The precipitate and crystals are the same as in (A).

26. K_2PtI_6. A dark-colored precipitate results.

27. Cs_2CdI_4. An amorphous precipitate separates immediately, from which appear thin plates collecting into clusters.

Birefringence	strong.
Extinction	parallel.
Elongation	indefinite.

28. *(A)* CdI_2. Crystals are obtained the same as in 27.

Illustration	figure 99.

(B) $CdBr_2$. Rectangular prisms are obtained in good number. Some of them form into clusters. Optical properties are the same as in 27.

(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. A copious non-crystalline precipitate is formed.

(B) K_2HgBr_4, *acidified.* Star-like crystals are formed almost at once. Pointed prisms collect in clusters of four and more units. The thinner forms give the shimmering colors due to thin films.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	0,2 mg./ml.
Illustration	figure 105.

30. $K_2Hg(SCN)_4$. An amorphous precipitate is obtained, from which, very shortly, a number of colorless thin irregular plates are formed,

together with a number of leaf-like dendritic forms. The latter are eliminated in the presence of a slight excess of acetic acid. Optical data are given for the plates.

Birefringence	weak.
Extinction	parallel.
Elongation	indefinite.
Illustration	figure 109.

31. *Potassium thallic iodide.* A copious red precipitate separates, in which a few long rods and a number of irregular spherulites may be noted. The spherulites are too irregular for optical characterization.

Illustration	figure 110.

32. *(A)* H_2SnCl_6. A precipitate is obtained composed of symmetrical spherulites of small well-formed prisms.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Illustration	figure 114.

(B) $H_2SnCl_6 + KBr$. Results are obtained as in (A) except the test is more sensitive.

33. $HSbCl_4$. Almost at once, numbers of dark-colored aggregates of fine, well-formed needles result. They have a high refractive index, and generally give almost perfect spherulites. Strychnine is the only alkaloid studied which yields a crystalline test form with this reagent.

Birefringence	strong; a polarization cross is obtained.
Extinction	parallel.
Elongation	negative.
Limiting concentration	0,3 mg./ml.
Illustration	figure 115.

34. $MnSO_4 + NH_4SCN$. Crystals are produced similar to the simple strychnine thiocyanate. They consist of long needles and pointed prisms.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.

35. $Co(NO_3)_2 + NH_4SCN$. Crystals of the simple thiocyanate result as in 34.

36. $Cr_2(SO_4)_3 + NH_4SCN$. Crystals of the simple thiocyanate result as in 34.

37. $NiSO_4 + NH_4SCN$. Crystals of the simple thiocyanate result as in 34.

38. $Na_3Co(NO_2)_6$. A copious turbidity results at once, from which, clusters of well-formed, slant-ended prisms crystallize.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.

39. *(A)* K_2PdBr_4. A crystalline precipitate results at once. It is composed of orange-colored needles in groups.

Birefringence	weak.
Other optical data	difficult to determine.
Illustration	figure 129.

(B) $PdCl_2$ *in HBr.* Results are obtained as in (A).

40. Na_2SnI_4. A precipitate is formed composed of short needles. Longer forms grow out of the mass on standing.

Birefringence	weak.
Other optical data	difficult to determine.
Illustration	figure 139.

41. *Diazo reaction.* No change.

Characteristic Test Forms

Of all the alkaloids studied, the greatest number of crystalline test forms were obtained with strychnine. The following reagents gave crystals with strychnine only: $HSbCl_4$, potassium acid phthalate, potassium antimonyl tartrate, and ammonium vanadate. Of these, the antimony chloride derivative is considered the most specific. The antimonyl tartrate derivative is unusual in that it is the only crystalline precipitate obtained in this study, that forms apparently isotropic crystals.

Caffeine

The test solution was prepared by dissolving 109 mg. of caffeine, $C_8H_{10}O_2N_4 \cdot H_2O$, in 10 ml. of distilled water, which gives a solution containing 10 mg. of the base per milliliter. The alkaloid used was tested for purity and was found to meet the standards of the U. S. Pharmacopeia X.

1. Br_2 *in* $NaBr$. A light-yellow precipitate forms, from which there soon appear golden-yellow aggregates of four and six-sided plates. They dissolve as the bromine evaporates from the solution. Best results are obtained by warming the test drop which has been strongly acidified with H_2SO_4.

Profile angle on plate (smaller)	approx. 74°.
Birefringence	strong.
Extinction	parallel.
Elongation	positive or negative.
Limiting concentration	1 mg./ml.
Illustration	figure 3.

2. ICl_3. A clear yellow solution results.
3. *(A)* $HClO_4$. No change.
   (B) $NaClO_4$. No change.
4. $Na_2B_4O_7$. No change.
5. NH_4VO_3. No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* No change.
8. *Sodium veronalate.* No change.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.
11. *KBr.* No change.
12. *(A)* $SnCl_2$. No change.
    (B) $SnBr_2$. No change.
13. $TiCl_3$. No change.
14. $BiCl_3$. No change.
15. *Potassium antimonyl tartrate.* No change.
16. $AsCl_3$. No change.
17. *Mercurochrome.* No change.
18. $NaAgI_2$. No change.
19. *(A)* $KAuI_2$. There results at once a precipitate of black irregular prisms. They collect into groups with serrated, irregular outlines. They do not transmit light.

Limiting concentration	0,5 mg./ml.
Illustration	figure 50.

(B) $HAuI_2$. A copious precipitation occurs, from which a large number of small black squares appear. They do not transmit light.

20. *(A)* $NaAuBr_4$. Almost immediately, sheaves and clusters of needles are formed in large numbers.

Dichroism	yellow to yellow-brown.
Birefringence	weak.
Extinction	parallel.
Elongation	negative.

(B) $HAuBr_4$. An orange precipitate appears which soon forms small spherulites and many clumps of brown irregular prisms. Single prisms also occur. The larger forms do not transmit light, the smaller are weakly birefringent, but are too irregular for the determination of the other optical data. The spherulites are of the same type, though smaller, as those described under (A). Optical data for these are the same as in (A). *Rosenthaler*[24] describes the form of this precipitate.

Illustration	figure 58.

21. $IrCl_4$. No change.
22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. No change occurs at first, but on standing, a few yellow branching leaflets appear along the side of the drop.

Birefringence	weak.
Other optical data	crystals too poorly formed for determination.
Illustration	figure 75.

25. *(A)* H_2PtCl_6 *in 20% HBr.* No change is observed at first. On standing, a few brown aggregates appear, composed of rectangular units.

Dichroism	yellow-brown to brown.
Other optical data	crystals too poorly formed for determination.
Illustration	figure 88.

(B) H_2PtCl_6 *in 5% HBr.* Results are obtained as in (A).

(C) Na_2PtBr_6. Results are obtained as in (A). Crystals are more numerous.

26. K_2PtI_6. From the clear solution, on standing and after scratching the slide, numbers of small dark-brown rectangular plates appear. Some of them are oriented in clusters. These are also obtained in acid solution. The larger crystals do not transmit light. Optical data are given for the smaller ones. *Amelink*[12] describes the form of this precipitate.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Limiting concentration	1 mg./ml.
Illustration	figure 91.

27. Cs_2CdI_4. No change.

28. *(A)* CdI_2. No change.
(B) $CdBr_2$. No change.
(C) $Cd(NO_3)_2 + NH_4SCN$. No change.
(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. No change.
(B) K_2HgBr_4, *acidified.* No change.

30. $K_2Hg(SCN)_4$. No change.

31. *Potassium thallic iodide.* A turbidity forms immediately.

32. *(A)* H_2SnCl_6. No change.
(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. No change.

35. $Co(NO_3)_2 + NH_4SCN$. No change.

36. $Cr_2(SO_4)_3 + NH_4SCN$. No change.

37. $NiSO_4 + NH_4SCN$. No change.

38. $Na_3Co(NO_2)_6$. No change.

39. *(A)* K_2PdBr_4. On standing, a number of very small needles are formed, some collecting into clusters.

Birefringence	weak.
Extinction	parallel.
Elongation	negative.
Illustration	figure 130.

(B) $PdCl_2$ *in HBr.* Crystals similar in form and optical properties to those in (A) are obtained. Crystals are formed more readily with (B), however.

40. Na_2SnI_4. No change.

41. *Diazo reaction.* A turbidity forms.

Characteristic Test Forms

Caffeine possesses little tendency toward formation of insoluble precipitates with the alkaloid reagents. The most useful test forms were obtained with the alkaloid reagents containing bromine or iodine. The most specific test is given by bromine in NaBr. None of the alkaloids studied, which produced crystalline precipitates with this reagent, gave the hexagonal forms noted here. The platinic iodide and gold bromide tests are good, although less specific.

Theobromine

The test solution was prepared by adding just sufficient 0,5 *N* NaOH to dissolve 100 mg. of theobromine and then diluting the resulting solution to 10 ml. with distilled water. This gave a solution containing 10 mg. of the alkaloid per milliliter. The tests described by *Amelink*[12] for theobromine were obtained on this solution.

1. Br_2 *in NaBr.* On stirring the test drop, acidified with H_2SO_4, a number of long pointed needles appear, singly, in sheaves and in clusters. A distinctly acid solution aids in crystal formation.

Birefringence	strong.
Extinction	parallel.
Elongation	negative.
Limiting concentration	0,5 mg./ml.
Illustration	figure 5.

2. ICl_3. Yellow, irregular, prismatic forms are obtained on standing.

Birefringence	weak.
Extinction	parallel.
Elongation	crystals too poorly formed for determination.
Illustration	figure 9.

3. *(A)* $HClO_4$. No change.
(B) $NaClO_4$. No change.

4. $Na_2B_4O_7$. No change.

5. NH_4VO_3. No change.

6. *Potassium anthraquinone sulfonate.* No change.

7. *Potassium xanthate.* No change.

8. *Sodium veronalate.* No change.

9. *Cupferron.* A colorless amorphous precipitate forms.

10. *Potassium acid phthalate.* No change.

11. *KBr.* No change.

12. $SnCl_2$. A copious colorless precipitate is formed. It is composed of tiny grains which are weakly birefringent.

13. $TiCl_3$. No change.

14. $BiCl_3$. No change.

15. *Potassium antimonyl tartrate.* Poorly defined, dumbbell-shaped crystals form on standing.

16. $AsCl_3$. No change.

17. *Mercurochrome.* No change.

18. $NaAgI_2$. No change.

19. *(A)* $KAuI_2$. A dark-colored amorphous precipitate results in the test drop.

(B) $HAuI_2$. One obtains immediately a number of small black rectangular prisms and rhombs. The prisms form somewhat irregular clusters. These crystals are soluble in alcohol, which, on evaporation, gives crystals similar to the above but more skeletal in shape. They do not transmit light.

Illustration ..... figure 51.

20. *(A)* $NaAuBr_4$. One obtains a faint precipitate, which crystallizes into brown hexagonal plates and rhombs. Some of the plates appear almost rectangular.

Dichroism	brown to yellow-brown.
Birefringence	weak.
Extinction	parallel (or symmetrical).
Elongation	positive or negative.

(B) $HAuBr_4$. A red precipitate results which soon crystallizes into dendritic aggregates of plates. The fundamental form seems to be an elongated hexagonal prism. A few symmetrical spherulites of needles form.

Dichroism	brown to yellow-brown.
Birefringence	weak; a polarization cross is obtained on the spherulites.
Extinction	parallel or symmetrical.
Elongation	negative (on elongated prisms).
Limiting concentration	0,3 mg./ml.
Illustration	figure 51.

21. $IrCl_4$. Rounded irregular dark-colored masses form on standing.

22. $RhCl_3$. Results similar to the foregoing are noted.

23. $RuCl_3$. Results similar to those with rhodium are obtained.

24. Na_2OsCl_6. A few rounded irregular yellow-colored masses develop on standing.

25. *(A)* H_2PtCl_6 *in 20%* HBr. An amorphous orange precipitate forms.

(B) H_2PtCl_6 *in 5%* HBr. An amorphous precipitate forms which on standing gives a few dumbbell-like irregular crystals.

(C) Na_2PtBr_6. Results are obtained as in (B).

26. K_2PtI_6. Tiny grains are obtained on standing.

27. Cs_2CdI_4. A slight precipitate composed of tiny grains is formed.

28. *(A)* CdI_2. A non-crystalline precipitate is formed.

(B) $CdBr_2$. A non-crystalline precipitate is formed.

(C) $Cd(NO_3)_2 + NH_4SCN$. No change.

(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. A gummy colorless precipitate results.

(B) K_2HgBr_4, *acidified*. A non-crystalline precipitate results.

30. $K_2Hg(SCN)_4$. No change.

31. *Potassium thallic iodide.* A dark-colored oil is produced.

32. *(A)* H_2SnCl_6. No change.

(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. No change.

35. $Co(NO_3)_2 + NH_4SCN$. No change.

36. $Cr_2(SO_4)_3 + NH_4SCN$. No change.

37. $NiSO_4 + NH_4SCN$. No change.

38. $Na_3Co(NO_2)_6$. Dumbbell-shaped crystals form on standing.

39. *(A)* K_2PdBr_4. An amorphous precipitate forms.

(B) $PdCl_2$ *in* HBr. Results are as in (A).

40. Na_2SnI_4. No change.

41. *Diazo reaction.* No change.

Characteristic Test Forms

Theobromine gives insoluble precipitates with many acidic radicals. Therefore precipitates are obtained with many of the reagents employed. The form of these precipitates is not characteristic. The long needles obtained with bromine in NaBr may be considered as the most specific test observed in this investigation. The crystalline form is distinctive and especially well suited for differentiating between caffeine and theobromine. The gold iodide and gold bromide tests are useful but less specific.

Nicotine

The test solution was prepared by dissolving 100 mg. of nicotine in 10 ml. of distilled water. This solution gave the tests described by *Amelink*[12] for nicotine.

1. *Br_2 in NaBr.* A slight yellow precipitate is obtained. It redissolves on standing.
2. *ICl_3.* No change.
3. *(A) $HClO_4$.* No change.
   (B) $NaClO_4$. No change.
4. *$Na_2B_4O_7$.* No change.
5. *NH_4VO_3.* No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* No change.
8. *Sodium veronalate.* No change.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.
11. *KBr.* No change.
12. *(A) $SnCl_2$.* No change.
    (B) $SnBr_2$. No change.
13. *$TiCl_3$.* No change.
14. *$BiCl_3$.* No change.
15. *Potassium antimonyl tartrate.* No change.
16. *$AsCl_3$.* No change.
17. *Mercurochrome.* No change.
18. *$NaAgI_2$.* No change.
19. *(A) $KAuI_2$.* On standing some time, the initial dark-colored precipitate crystallizes into large dark-brown groups of overlapping plates. The plates are oblong and do not transmit light.

    Limiting concentration ..... 0,5 mg./ml.
    Illustration ..... figure 52.

    (B) $HAuI_2$. Results are obtained as in (A).
20. *(A) $NaAuBr_4$.* A red-colored precipitate is formed immediately. It is composed of tiny right-angled plates and squares, barely visible at a magnification of 200 ×. This precipitate has been described by *Amelink*.[12] If a drop of alcohol be added to the precipitate, there are formed much larger light-brown clusters of prisms arranged in leaf-like forms with serrated edges.

    Dichroism ..... yellow-brown to brown (noticeable especially when recrystallized from alcohol).
    Birefringence ..... weak.
    Extinction ..... oblique; these are the only gold bromide crystals, besides cocaine, having oblique extinction.

Elongation ..... negative.
Limiting concentration ..... 1 mg./ml.
Illustration ..... figure 60.

(B) $HAuBr_4$. Results are obtained as in (A).

21. $IrCl_4$. No change.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. No change.

25. *(A)* H_2PtCl_6 *in 20% HBr*. Immediately, there is produced a number of tiny rhombs and prisms possessing a high refractive index. They are insoluble in alcohol. Crystals are best obtained from $^1/_4$% solution of the alkaloid.

Dichroism ..... yellow to brown.
Birefringence ..... weak.
Extinction ..... oblique and parallel.
Elongation ..... positive or negative.
Limiting concentration ..... 0,5 mg./ml.
Illustration ..... figure 89.

(B) H_2PtCl_6 *in 5% HBr*. Results are obtained as in (A) but crystallization takes place more readily.

(C) Na_2PtBr_6. Crystals are obtained as in (B).

26. K_2PtI_6. A black amorphous precipitate forms which, on standing, crystallizes into tiny cubes and rectangular plates. They do not transmit light. The form of this precipitate has been described by *Rosenthaler*.[24]

Illustration ..... figure 92.

27. Cs_2CdI_4. No change.

28. *(A)* CdI_2. No change.

(B) $CdBr_2$. No change.

(C) $Cd(NO_3)_2 + NH_4SCN$. A voluminous precipitate is produced which, on standing, yields a number of irregular spheres. These finally develop into colorless aggregates of overlapping plates. The ends are usually pointed. The crystals are slightly soluble in alcohol. Optical data are given for the plates.

Birefringence ..... strong.
Extinction ..... symmetrical.
Elongation ..... negative.
Limiting concentration ..... 5 mg./ml.
Illustration ..... figure 100.

(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. From the initial amorphous precipitate, one soon obtains a very good collection of fine irregular aggregates of laminated plates and needles. On standing, the finer needles broaden out into plates.

Birefringence	strong.
Extinction	oblique, average of 10°; this is the only derivative with this reagent showing oblique extinction.
Elongation	positive.
Limiting concentration	1 mg./ml.
Illustration	figure 104.

(B) K_2HgBr_4, *acidified.* Results are obtained as in (A).

30. $K_2Hg(SCN)_4$. A colorless precipitate forms immediately.

31. *Potassium thallic iodide.* A brown precipitate is formed at once.

32. *(A)* H_2SnCl_6. No change.
(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. There soon develop a number of elongated, pointed prisms of high refractive index. The crystals are more readily produced by stirring the test drop.

Birefringence	strong.
Extinction	parallel.
Elongation	positive.
Illustration	figure 117.

35. $Co(NO_3)_2 + NH_4SCN$. On standing for two or three minutes, a large number of pointed prisms, rhombs, and hexagonal plates are obtained; rectangular plates may also be noted. These often develop little notches in one or both ends of the crystal. On growing to large size, the crystals acquire a pinkish cast.

Birefringence	strong.
Extinction	parallel on oblong plates; oblique, approx. 12°, on pointed prisms.
Elongation	positive, larger oblong plates; negative, pointed prisms.
Limiting concentration	5 mg./ml.
Illustration	figure 124.

36. $Cr_2(SO_4)_3 + NH_4SCN$. A slight turbidity develops on standing.

37. $NiSO_4 + NH_4SCN$. One obtains at once a precipitate of irregular prismatic aggregates.

Birefringence	weak.
Other optical data	crystals are too irregular for determination.
Illustration	figure 126.

38. $Na_3Co(NO_2)_6$. No change.

39. *(A)* K_2PdBr_4. A yellow precipitate forms immediately.
(B) $PdCl_2$ *in* HBr. An orange precipitate forms.

40. Na_2SnI_4. No change.

41. *Diazo reaction.* A yellow oil separates.

Characteristic Test Forms

Nicotine, like brucine, is characterized by its tendency toward formation of complex metallo-thiocyanates. Crystalline precipitates of this type are obtained with cadmium, cobalt, manganese and nickel. The cobalt compound is most useful for identification of the alkaloid. A number of the crystals obtained with this alkaloid exhibit oblique extinction and, among these the potassium mercuric bromide precipitate is the only one of all the alkaloid precipitates produced by this reagent, on which this property has been observed.

Atropine

The test solution was prepared by dissolving 120 mg. of atropine sulfate, $(C_{17}H_{23}O_3N)_2H_2SO_4 \cdot H_2O)$, in 10 ml. of distilled water. This gave a solution containing 10 mg. of the alkaloid per milliliter. The alkaloid used was tested for purity and was found to meet the standards of the U. S. Pharmacopeia X.

1. *Br_2 in NaBr.* Almost immediately, a large number of yellow needles and pointed prisms are obtained. Many of the latter have notched ends which are easily observed at a magnification of 40 diameters. This is a sensitive and useful crystalline derivative for the identification of atropine. Optical data are given for the prisms.

Birefringence	strong.
Extinction	parallel.
Elongation	positive; these are the only positively elongated crystals obtained with this reagent.
Limiting concentration	0,1 mg./ml.
Illustration	figure 2.

2. *ICl_3.* A yellow turbidity results.
3. *(A) $HClO_4$.* No change.
   (B) $NaClO_4$. No change.
4. *$Na_2B_4O_7$.* No change.
5. *NH_4VO_3.* No change.
6. *Potassium anthraquinone sulfonate.* No change.
7. *Potassium xanthate.* No change.
8. *Sodium veronalate.* No change.
9. *Cupferron.* No change.
10. *Potassium acid phthalate.* No change.

11. *KBr*. No change.

12. *(A)* $SnCl_2$. No change.

(B) $SnBr_2$. No change.

13. $TiCl_3$. No change.

14. $BiCl_3$. No change.

15. *Potassium antimonyl tartrate*. No change.

16. $AsCl_3$. No change.

17. *Mercurochrome*. A copious red precipitate forms.

18. $NaAgI_2$. No change.

19. *(A)* $KAuI_2$. A black precipitate is formed which ultimately yields irregular black grain like crystals. They do not transmit light.

Illustration ..... figure 53.

(B) $HAuI_2$. Results are obtained as in (A).

20. *(A)* $NaAuBr_4$. A yellow-colored precipitate forms immediately.

(B) $HAuBr_4$. An orange-colored precipitate forms immediately; on warming, it collects into oily drops.

21. $IrCl_4$. No change.

22. $RhCl_3$. No change.

23. $RuCl_3$. No change.

24. Na_2OsCl_6. No change.

25. *(A)* H_2PtCl_6 *in 20% HBr*. An orange-colored precipitate is formed.

(B) H_2PtCl_6 *in 5% HBr*. An orange-colored precipitate results.

(C) Na_2PtBr_6. An orange-colored precipitate results.

26. K_2PtI_6. A black-colored precipitate forms.

27. Cs_2CdI_4. No change.

28. *(A)* CdI_2. A faint precipitate is obtained.

(B) $CdBr_2$. No change.

(C) $Cd(NO_3)_2 + NH_4SCN$. No change.

(D) $CdCl_2$. No change.

29. *(A)* K_2HgBr_4. A colorless turbidity is produced.

(B) K_2HgBr_4, *acidified*. A colorless turbidity is produced.

30. $K_2Hg(SCN)_4$. A copious turbidity is obtained.

31. *Potassium thallic iodide*. A copious red turbidity forms which collects into drops.

32. *(A)* H_2SnCl_6. No change.

(B) $H_2SnCl_6 + KBr$. No change.

33. $HSbCl_4$. No change.

34. $MnSO_4 + NH_4SCN$. A copious turbidity results.

35. $Co(NO_3)_2 + NH_4SCN$. A copious turbidity results.

36. $Cr_2(SO_4)_3 + NH_4SCN$. A copious turbidity results.

37. $NiSO_4 + NH_4SCN$. A slight turbidity forms on standing.

38. $Na_3Co(NO_2)_6$. No change.

39. *(A)* K_2PdBr_4. An orange-colored precipitate is obtained.
(B) $PdCl_2$ *in* HBr. An orange-colored precipitate is obtained.

40. Na_2SnI_4. No change.

41. *Diazo reaction.* A copious yellow-colored oil is obtained.

Characteristic Test Forms

Atropine gives relatively few precipitation reactions. Bromine in NaBr produces a characteristic and useful crystalline test form, especially in conjunction with the sign of elongation of the crystals obtained.

Summary of Experimental Results

The findings on the analytical usefulness and efficiency of the reagents investigated are summarized in the following. The reagents are discussed one by one in the order adopted for this presentation.

1. Br_2 *in* $NaBr$. The reagent is a general precipitant for all of the alkaloids studied. Crystalline precipitates, suited for microscopic study, are obtained with six alkaloids. Of these, the most distinctive forms are produced with theobromine, caffeine, and atropine. Only the last gives a precipitate, the crystals of which show positive elongation.

2. ICl_3. Amorphous precipitates are obtained with most alkaloids. The crystallizations resulting with one or two of the alkaloids are of little value for the purpose of identification.

3. *(A)* $HClO_4$. Four distinctly crystalline derivatives are obtained with this reagent. They are produced with strychnine, brucine, morphine, and cocaine. The precipitates are distinctive especially when the profile angles and the optical data are considered.

(B) NH_4ClO_4. Three additional alkaloids yield crystals with this reagent, namely, novocaine, cinchonine, and quinidine. The crystals of the novocaine perchlorate are the most useful, providing that the optical data are utilized.

4. $Na_2B_4O_7$. The free alkaloid bases are obtained. Their appearances differ slightly from those reported by *Stephenson*,[11] who used sodium carbonate as reagent.

5. NH_4VO_3. Precipitates are obtained with a few alkaloids; crystals separate with strychnine only. The forms of the strychnine precipitate are, however, not very characteristic and other reagents appear preferable for the identification of this alkaloid.

6. *Potassium anthraquinone sulfonate.* Crystalline sulfonates were obtained with heroine, cinchonidine, quinidine, quinine, and strychnine. The large prisms of the quinidine sulfonate are the only crystals of this type obtained with the reagent. As to the other alkaloids mentioned, their sulfonate precipitates are similar in appearance and difficult to distinguish one from the other.

7. *Potassium xanthate.* Only brucine and strychnine give crystalline xanthates. The isopropyl and the butyl xanthates have been investigated, but they offer no particular advantages.

8. *Sodium veronalate.* No precipitate of characteristic crystalline form has been found.

9. *Cupferron.* A crystalline precipitate has been observed with beta eucaine only. The crystals are not particularly well-developed.

10. *Potassium acid phthalate.* Only one crystalline acid phthalate was obtained, that of strychnine, which grows in well-formed characteristic crystals.

11. *KBr.* Crystals were observed in the precipitates with beta eucaine, codeine, and stovaine. The determination of the silhouette angle is useful for the identification of the crystals produced with beta eucaine. In addition to the alkaloids listed above, some others may precipitate if the KBr concentration is increased above that produced by the reagent solution.

12. *(A)* $SnCl_2$. The reagent yields crystals with strychnine, brucine, beta eucaine, and cocaine. Because of the oblique extinction exhibited, the crystals with beta eucaine are most characteristic. The cocaine derivative, which does not crystallize well, is the only other one showing oblique extinction.

(B) $SnBr_2$. Approximately the same results are obtained as with the chloride (A). It may be mentioned, however, that cocaine gives well-developed crystals with $SnBr_2$.

13. $TiCl_3$. Crystalline derivatives suitable for slide tests result with strychnine, brucine, and papaverine. The three alkaloids can be distinguished by the habit of the crystals produced with the reagent.

14. $BiCl_3$. Strychnine and brucine give crystals which are characteristic if the sign of elongation is considered.

15. *Potassium antimonyl tartrate.* Strychnine is the only alkaloid producing separation of crystals. They appear isotropic when examined between crossed nicols. This is the sole isotropic test form met with in the course of this investigation.

16. $AsCl_3$. No crystalline precipitate was obtained with any of the alkaloids studied.

17. *Mercurochrome.* This reagent precipitates nearly all of the alkaloids studied. No crystalline phases, such as are formed with the inorganic mercury halides, were observed.

18. $NaAgI_2$. The reagent yields a very characteristic crystalline iodo-argentate with cocaine. The only other crystalline precipitates, obtained with this reagent, are the simple iodides of quinidine, strychnine, and brucine. The cocaine iodo-argentate is easily recognized by the habit of its crystals and their oblique extinction.

19. *(A)* $KAuI_2$. The gold iodo complex is a sensitive general precipitant. With certain alkaloids, as with caffeine and nicotine, the crystal forms of the precipitates are quite satisfactory for the purpose of microscopic identification.

(B) $HAuI_2$. In general, the observed crystal forms were similar to those produced by the potassium salt (A). $HAuI_2$, unlike $KAuI_2$, gives a crystalline precipitate with theobromine.

20. *(A)* $NaAuBr_4$. This reagent gives more sensitive tests than the corresponding chloro compound; the crystals of the precipitates are smaller than those of the chloraurates. Especially the caffeine bromaurate produces crystals which appear better suited for chemical microscopy than those of the chloro compound. Nicotine and cocaine are the only alkaloids whose bromaurates show oblique extinction. Quinidine is the only alkaloid investigated, which, on addition of $NaAuBr_4$ causes separation of crystals which possess positive elongation.

(B) $HAuBr_4$. In general, approximately the same results are obtained as with the sodium salt (A). Theobromine gives better crystals with $HAuBr_4$ than with $NaAuBr_4$.

21. $IrCl_4$. Iridium tetrachloride gives practically the same crystalline forms as the platinic bromide reagents (25). The crystals are usually brown and more soluble than the bromo-platinates. As a general statement one may say that the iridium and osmium complexes are especially useful if the corresponding platinum compounds are too insoluble for the development of well-formed crystals. Thus, narcotine iridium chloride forms crystals, while the chloroplatinate is reported as non-crystalline by *Amelink.*[12]

22 and 23. $RhCl_3$ and $RuCl_3$. The trichlorides of rhodium and ruthenium, both metals belonging to the sub-group of the platinum metals, differ materially from the chlorides of the main group in their behaviour toward alkaloids. As would be expected, the fact that few insoluble crystalline phases are obtained with the chlorides of rhodium and ruthenium increases the specificity of the tests observed. Both reagents give crystals with strychnine and brucine; in addition, ruthenium chloride produces a somewhat soluble crystalline precipitate with cocaine. This latter constitutes one of the more specific tests for cocaine because of the oblique extinction exhibited by the crystals of the precipitate.

24. Na_2OsCl_6. The osmate precipitates are yellow. The form of the crystals is very similar to that of the iridium precipitates (21).

25. *(A)*, *(B)*, and *(C)*. H_2PtCl_6 in *20%* HBr, H_2PtCl_6 in *5%* HBr, and Na_2PtBr_6. These reagents give tests of higher sensitivity than the generally used chloroplatinic acid. An analytically useful crystallization has been observed with dionine, for which no corresponding test with H_2PtCl_6 has been reported. In particular cases, the variation of the concentration of HBr or NaBr aids in producing crystals suitable for microscopic identification. The twig-like crystals obtained with cocaine constitute the most unusual crystalline form obtained with these bromoplatinate reagents. The shape, combined with the angle of extinction of the crystals, renders the test fairly specific for cocaine; besides, an unusually high sensitivity may be obtained by adding more NaBr to the test drop than is specified by the recipe for the reagent. Also, the crystals obtained with cinchonine are characteristic, since they are the only ones, obtained with the bromoplatinate reagents that show oblique extinction and negative elongation.

26. K_2PtI_6. In general, this reagent gives tests of remarkable sensitivity. Precipitates are obtained with all of the alkaloids studied, but only a few of the precipitates are suited for microscopic identification. The form of the crystals of the cinchonine precipitate is the most characteristic.

27. Cs_2CdI_4. Several alkaloids give crystalline precipitates with this reagent. It appears, however, that the crystals have essentially the same forms and optical properties as those obtained with CdI_2 alone (see below).

28. *(A)* CdI_2. A number of alkaloids produce crystals with this reagent, but, in general, the habit of the crystals is not especially characteristic. A specific test is obtained with codeine: the crystals of the codeine derivative are the only ones, obtained with this reagent, which

exhibit oblique extinction and negative elongation. The crystals of the morphine precipitate are the only ones possessing parallel extinction combined with definite negative elongation.

(B) $CdBr_2$. A number of those alkaloids which give precipitates with CdI_2 also yield crystals with $CdBr_2$. The derivative obtained with novocaine is analytically useful.

(D) $CdCl_2$. With heroine, crystallization occurs if the test drop is allowed to stand for some time. The crystals are, however, quite soluble.

29. *(A) K_2HgBr_4* and *(B) K_2HgBr_4, acidified.* Insoluble salts are produced with all of the alkaloids. Reagent (A) gives crystals suitable for chemical microscopy with morphine, nicotine, codeine, and brucine. The very slight birefringence of the morphine precipitate is useful for identification: the crystals produced with nicotine are the only ones obtained with the reagent which show oblique extinction. Reagent (B) produces crystals also with strychnine, dionine, and beta eucaine. The forms of the eucaine derivative exhibit oblique extinction.

30. *$K_2Hg(SCN)_4$.* This reagent is useful as a general precipitant. Crystallization results only with strychnine and brucine, but the crystals are not especially characteristic.

31. *Potassium thallic iodide.* The reagent yields amorphous precipitates with nearly all of the alkaloids studied and, since crystalline forms could not be obtained, it does not appear suited for chemical microscopy.

32. *(A) H_2SnCl_6.* Crystalline derivatives are obtained with those alkaloids which produce crystals with stannous chloride, i. e., with beta eucaine, cocaine, brucine, and strychnine. A tabulation of the optical properties of the crystals of these precipitates demonstrates the usefulness of this reagent.

Alkaloid:	Extinction:	Elongation:
Beta eucaine	oblique	negative
Cocaine	some parallel, some oblique	positive
Brucine	parallel	positive
Strychnine	parallel	negative

Extinction angle and sign of elongation can be rapidly determined and serve to increase the certainty of identification.

(B) $H_2SnCl_6 + KBr$. The crystals obtained resemble those formed with H_2SnCl_6; they are somewhat smaller than those of the corresponding chlorostannates.

33. $HSbCl_4$. Only with one alkaloid, strychnine, is a definitely crystalline precipitate obtained. Of all the reagents studied, $HSbCl_4$ is the most specific one for strychnine.

34. $MnSO_4 + NH_4SCN$, 35. $Co(NO_3)_2 + NH_4SCN$, 36. $Cr_2(SO_4)_3 + NH_4SCN$, and 28. *(C)* $Cd(NO_3)_2 + NH_4SCN$. Complex thiocyanates were obtained with nicotine and brucine, although not all of the reagents listed gave crystals with both alkaloids. The test for nicotine obtained with $Co(NO_3)_2 + NH_4SCN$ is the best representative of the whole series. Since the simple thiocyanates of some alkaloids are difficultly soluble, care was taken to compare the tests given by the above reagents with the crystals obtained on addition of NH_4SCN alone.

39. *(A)* K_2PdBr_4 and *(B)* $PdCl_2$ *in* HBr. Precipitates suitable for identification with the use of the microscope were obtained with four alkaloids: beta eucaine, brucine, strychnine, and caffeine. The habit of the crystals of these precipitates is, however, not particularly distinctive.

40. Na_2SnI_4. The iodostannite appears to be a more general precipitant than the tin chlorides. The habit of the crystals precipitated from solutions of several alkaloids does not show much variety, especially morphine and its derivatives produce nearly identical crystals. Most distinctive is the test obtained with cinchonidine.

Strychnine, brucine, and cocaine gave crystalline precipitates with the largest number of reagents, a fact which was also demonstrated in the work of *Stephenson*. *Fulton* has pointed out that a reagent is not likely to react with other alkaloids if it fails to produce difficultly soluble products with the above three bases of proven precipitating power. Consequently, when searching for new general alkaloid reagents, it would be advisable that those proposed be first tested with strychnine, brucine, and cocaine. If no precipitates result with these bases, the idea of establishing a general reagent may be discarded. In the present work it was shown, however, that the inability of a reagent to precipitate strychnine, brucine, and cocaine does not imply total lack of precipitating action upon all alkaloids. On the contrary, failure to precipitate the three most reactive alkaloids should invite an extension of the experiments to other bases in the hope of discovering a specific alkaloid reagent like cupferron, which gives a characteristic crystalline precipitate with beta eucaine but is without effect when added to solutions of the three most reactive bases.

Zusammenfassung.

Die Arbeit beschäftigt sich mit der systematischen Untersuchung des Verhaltens der auf Seite 250 aufgezählten, bei toxikologischen Untersuchungen häufiger angetroffenen Alkaloidbasen gegenüber 50 Reagenzien. Die auf dem Objektträger erhaltenen Niederschläge wurden mikroskopisch untersucht und gegebenenfalls durch die Bestimmung einfach und rasch zu erfassender Eigenschaften der Kristalle, wie Profilwinkel, Einfachbrechung, Doppelbrechung, Auslöschungswinkel, Pleochroismus, und Verhalten gegenüber dem Gipsblättchen weiters charakterisiert.

Eine Durchsicht der Liste der Reagenzien (S. 251 ff.) zeigt, daß außer altbekannten Alkaloidreagenzien eine größere Zahl von bisher wenig oder gar nicht zur Alkaloiderkennung benutzten Reagenzien studiert wurde. Eine systematische Untersuchung des Verhaltens einer möglichst großen Zahl der häufiger angetroffenen Basen erschien erforderlich, da die Spezifität einer Probe nur auf Grundlage der Kenntnis des Verhaltens des Reagens gegenüber allen anderen in Frage kommenden Stoffen sichergestellt werden kann.

Die zur Erkennung der Basen nützlichen Reaktionsbilder sind in Tafeln (S. 323 ff.), nach Reagenzien angeordnet, gesammelt. Der systematische Bericht der Untersuchungsbefunde (S. 256) ist nach den Alkaloidbasen eingeteilt. Eine kurze Zusammenfassung betreffend die für jede Base bestgeeigneten Nachweisverfahren ist jeweils am Ende des der Base gewidmeten Kapitels gegeben.

Die Nützlichkeit der studierten Reagenzien für die Erkennung von Alkaloidbasen wird zum Abschluß zusammenfassend besprochen (S. 315). Die Reagenzien Brom-Bromnatrium, Perchlorsäure, Kaliumbromid, Stannochlorid, Titanochlorid, Kaliumjodaurit, Natriumbromaurat, Platinbromwasserstoffsäure, Kaliumbrommercurat, Zinnchlorwasserstoffsäure und Palladiumbromwasserstoffsäure geben mit mehreren Basen kristalline Niederschläge, die durch Aussehen und Eigenschaften die Erkennung der Basen ermöglichen. Kaliumxanthat, Wismutchlorid, Rhodiumtrichlorid, Rutheniumtrichlorid und Cadmiumjodid erzeugen mit nur je zwei der untersuchten Alkaloidbasen gut kristallisierte Niederschläge, und die folgenden Reagenzien erscheinen durchaus spezifisch: Kupferron gibt nur mit β-Eucain einen kristallinen Niederschlag; primäres Kaliumphthalat und Kaliumantimonyltartrat erzeugen nur mit Strychnin Kristallisationen; Cocain ist das einzige Alkaloid, das ein kristallisiertes Jodargentat gab, und lediglich bei Strychnin konnte ein eindeutig kristalliner Niederschlag mit $HSbCl_4$ erhalten werden. *Fulton* hat darauf hingewiesen, daß Reagenzien, die mit Brucin, Strychnin und Cocain keine Fällungen geben, nicht als allgemeine Alkaloidreagenzien in Betracht gezogen werden können, da sie wahrscheinlich auch mit anderen Basen keine Niederschläge zu erzeugen imstande sein dürften. Es wird nun darauf hingewiesen, daß Reagenzien, die mit den obgenannten drei Alkaloiden versagen, doch studiert werden sollten, da die Möglichkeit besteht, daß sie mit einem anderen Alkaloid einen spezifischen Nachweis geben.

Résumé *(L).*

Le présent travail étudie systématiquement le comportement (signalé page 250) des alcaloides les plus courants en toxicologie, vis à vis de 50 réactifs.

Le précipité obtenu sur porte objet est examiné microscopiquement et éventuellement caractérisé par détermination simple et rapide des propriétés cristallines telles que le profil angulaire, la simple et double réfringence, l'angle d'extinction, le pleochroisme et son comportement en présence d'une lame de gypse.

L'examen de la liste (p. 251) révèle qu'un grand nombre de réactifs peu ou pas du tout utilisés jusqu'ici dans l'identification des alcaloides ont été étudiés à côté des réactifs usuels, bien connus. Une étude systématique du comportement du plus grand nombre possible des bases les plus courantes s'imposait, parce que la spécificité d'un essai n'est établie avec certitude que si l'on connait la façon dont se comporte le réactif vis à vis de toutes les autres substances qui interviennent dans l'essai.

Le Tableau (p. 323) donne tous les schémas de réaction nécessaires à l'identification des alcaloides, en prenant les réactifs comme base de classification.

L'exposé des résultats de la recherche est subdivisé d'après les bases alcaloidiques (p. 256).

Chaque chapitre se rapportant à un alcaloide déterminé se termine par un court résumé des procédés d'identification les mieux appropriés.

La justification de l'emploi des réactifs étudiés est finalement discutée (p. 315) sous une forme résumée.

Les précipités cristallins dont l'aspect et les propriétés permettent l'identification des bases, sont obtenus par les réactifs suivants: le bromo-bromure de sodium, l'acide perchlorique, le bromure de potassium, le chlorure stanneux et titaneux, l'iodoaurite de potassium, le bromoaurate de sodium, l'acide bromoplatinique, le bromomercurate de potassium, les acides chlorostannique et bromopalladique.

Les réactifs suivants ne donnent de précipité cristallin qu'avec deux bases alcaloides étudiées: le xanthate de potassium, le chlorure de bismuth, le trichlorure de rhodium, de ruthénium et l'iodure de cadmium. Les réactifs suivants sont apparus comme spécifiques: le cupferron ne donne de précipité cristallin qu'avec la b-Eucaine; le phtalate acide de potassium et le tartrate de potassium et d'antimonyle ne fournissent de précipité cristallin qu'avec la strychnine; la cocaine est le seul des alcaloides formant un iodoargentate et enfin, la strychnine a donné un précipité cristallin avec $HSbCl_4$. *Fulton* avait avancé que les réactifs ne précipitant pas avec la brucine, la strychnine et la cocaine ne pouvaient pas être considérés comme des réactifs généraux des alcaloides, parce que vraisemblablement ils se comportent de même avec d'autres alcaloides. Le présent travail démontre la nécessité d'étudier des réactifs, même s'ils ne précipitent pas ces trois alcaloides, parce qu'ils peuvent avec d'autres alcaloides, donner lieu à des réactions spécifiques.

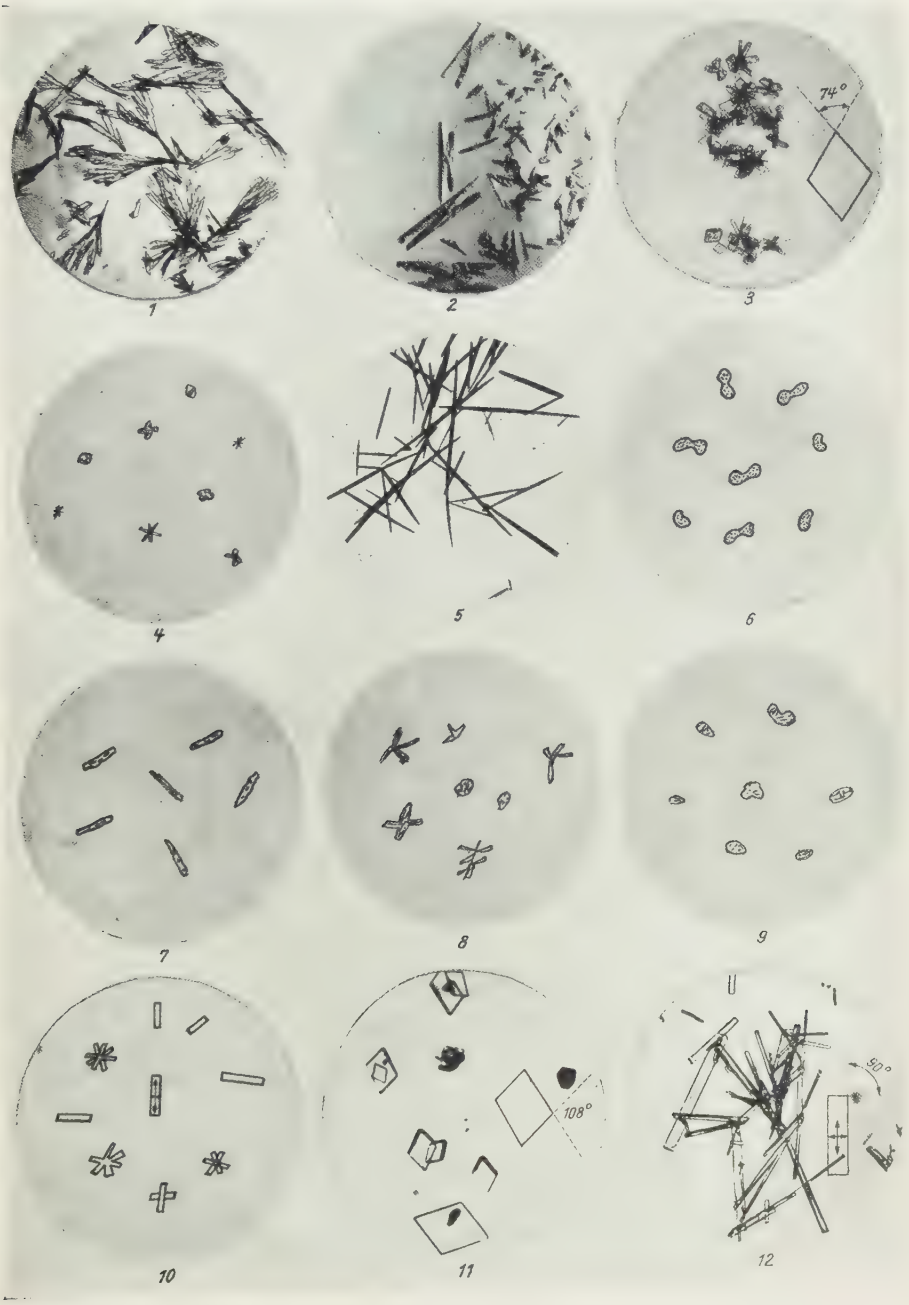

Table I

Test Forms with Br_2 in NaBr: Fig. 1. Novocaine, Fig. 2. Atropine, Fig. 3. Caffeine, Fig. 4. Brucine, Fig. 5. Theobromine. *Test Forms with ICl_3:* Fig. 6. Codeine, Fig. 7. Morphine, Fig 8. Strychnine, Fig. 9. Theobromine. *Test Forms with $HClO_4$:* Fig. 10. Cocaine, Fig. 11. Brucine, Fig. 12. Strychnine.

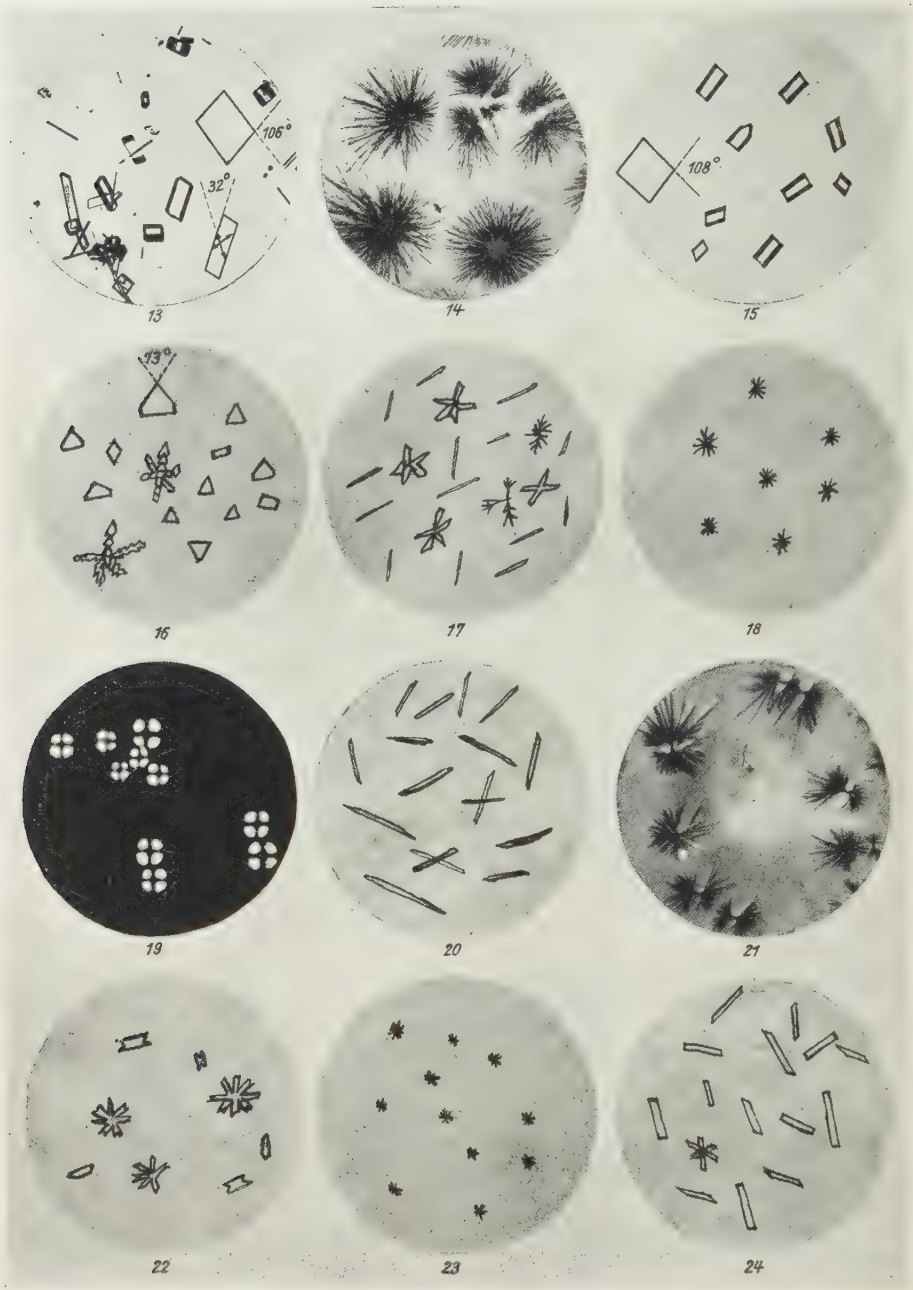

Table II

Test Forms with NH_4ClO_4*:* Fig. 13. Novocaine, Fig. 14. Cocaine, Fig. 15. Cinchonine, Fig. 16. Quinidine. *Test Form with* NH_4VO_3*:* Fig. 17. Strychnine. *Test Forms with* $Na_2B_4O_7$*:* Fig. 18. Cinchonine, Fig. 19. Cinchonidine (between crossed nicols), Fig. 20. Quinidine, Fig. 21. Narcotine, Fig. 22. Papaverine, Fig. 23. Brucine, Fig. 24. Strychnine.

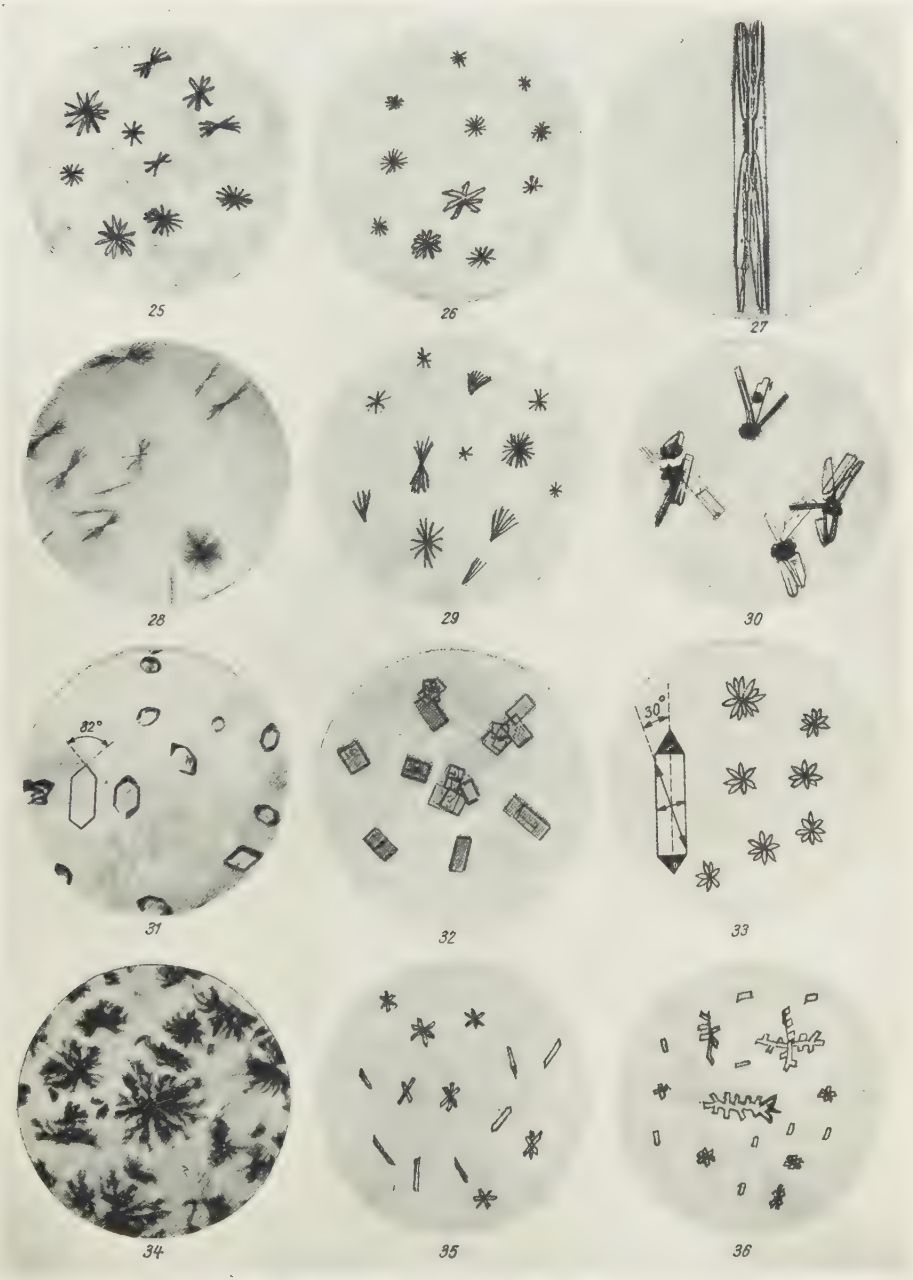

Table III

Test Forms with Potassium Anthraquinone Sulfonate: Fig. 25. Heroine, Fig. 26. Cinchonidine, Fig. 27. Quinidine, Fig. 28. Quinine, Fig. 29. Strychnine. *Test Form with Cupferron:* Fig. 30. Beta Eucaine. *Test Forms with KBr:* Fig. 31. Beta Eucaine, Fig. 32. Stovaine. *Test Forms with* $SnCl_2$: Fig. 33. Beta Eucaine, Fig. 34. Cocaine, Fig. 35. Brucine, Fig. 36. Strychnine.

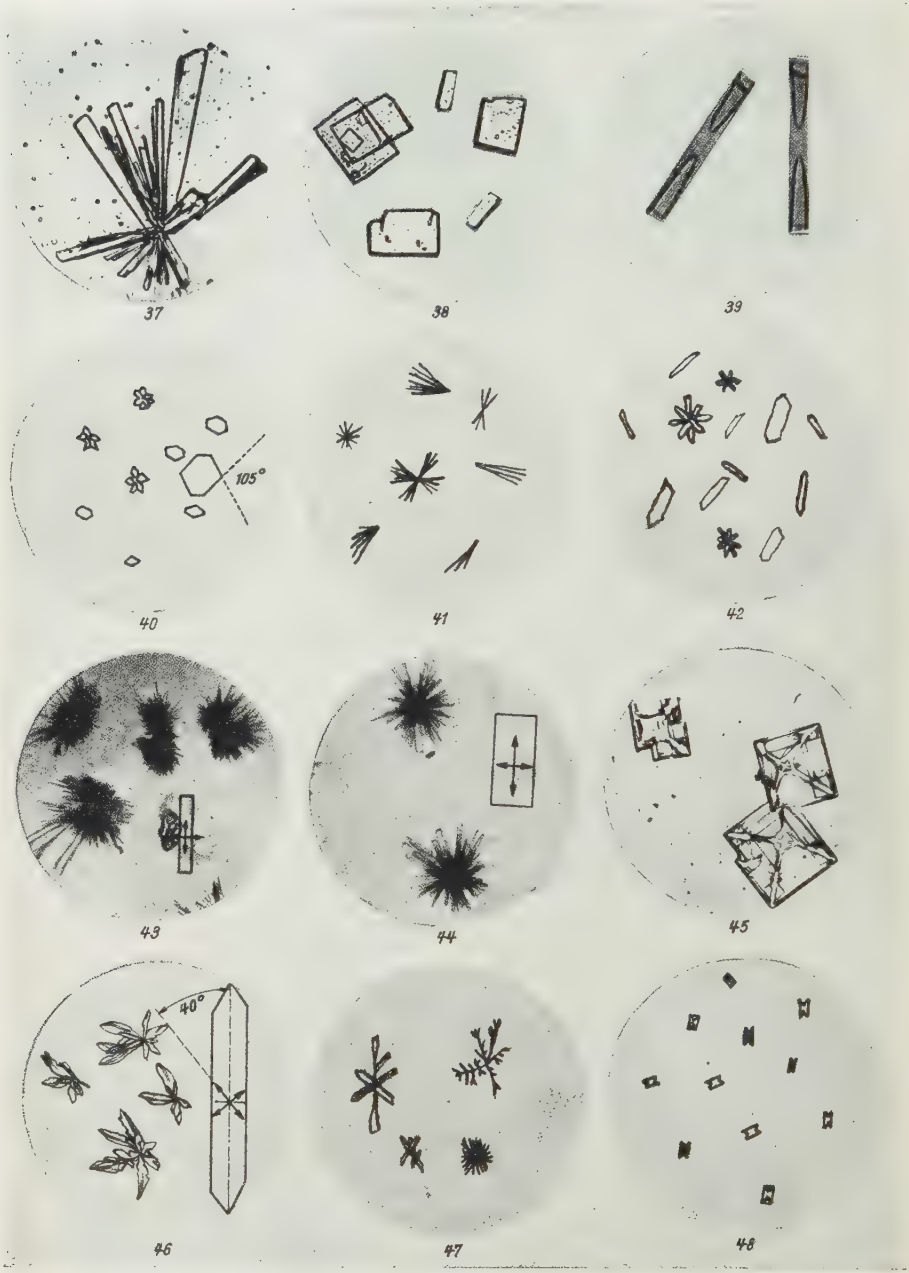

Table IV

Test Forms with Potassium Xanthate: Fig. 37. Strychnine, Fig. 38. Brucine. *Test Form with Potassium Acid Phthalate:* Fig. 39. Strychnine. *Test Forms with $TiCl_3$:* Fig. 40. Papaverine, Fig. 41. Strychnine, Fig. 42. Brucine. *Test Forms with $BiCl_3$:* Fig. 43. Brucine, Fig. 44. Strychnine. *Test Form with Potassium-Antimonyl Tartrate:* Fig. 45. Strychnine. *Test Form with $NaAgI_2$ Reagent:* Fig. 46. Cocaine, *Test Forms with $KAuI_2$ Reagent:* Fig. 47. Novocaine, Fig. 48. Stovaine.

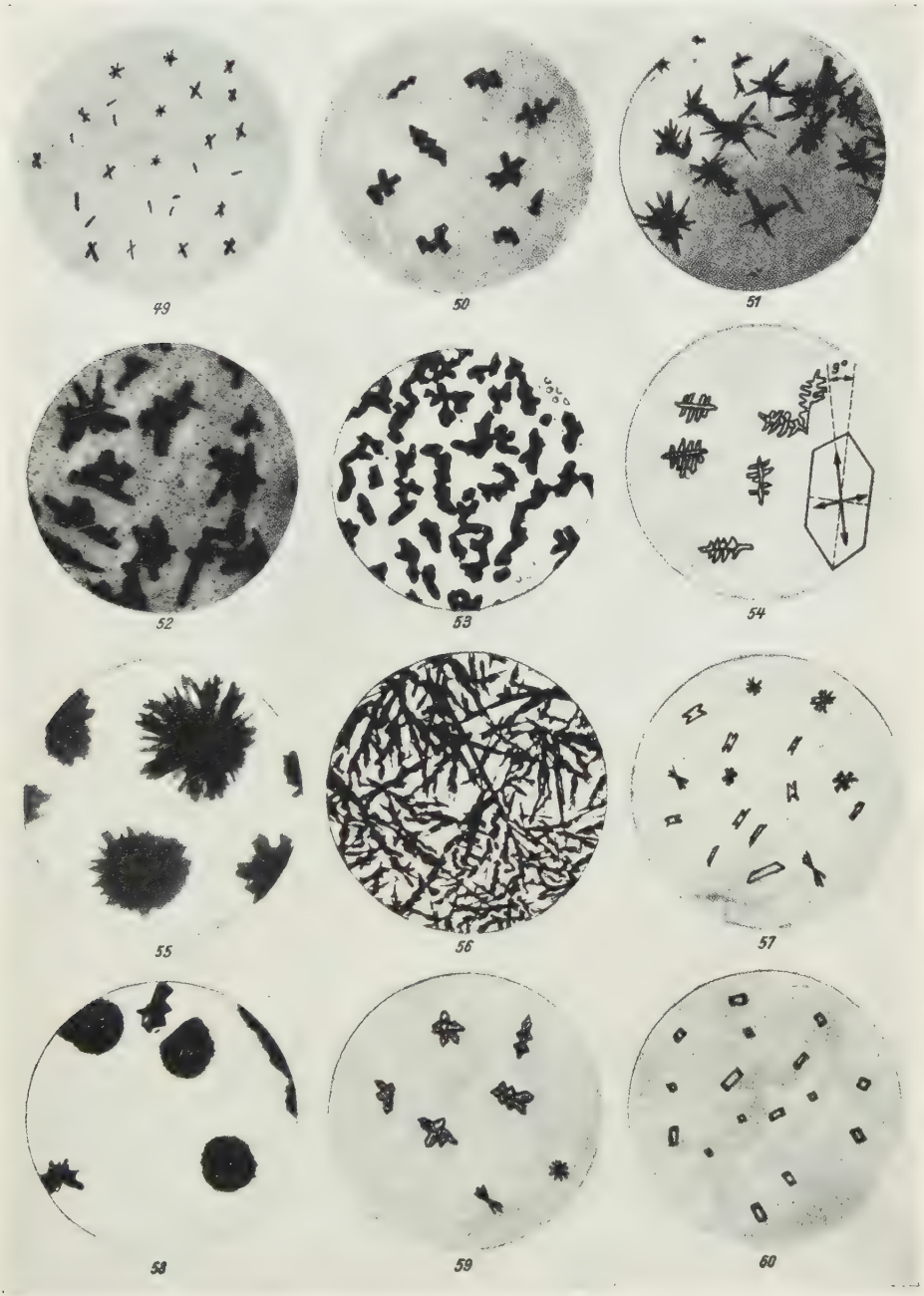

Table V

Test Forms with $KAuI_2$ Reagent: Fig. 49. Strychnine, Fig. 50. Caffeine, Fig. 51. Theobromine, Fig. 52. Nicotine, Fig. 53. Atropine. *Test Forms with $HAuBr_4$ Reagent:* Fig. 54. Cocaine, Fig. 55. Novocaine, Fig. 56. Stovaine, Fig. 57. Quinidine, Fig. 58. Caffeine, Fig. 59. Theobromine, Fig. 60. Nicotine.

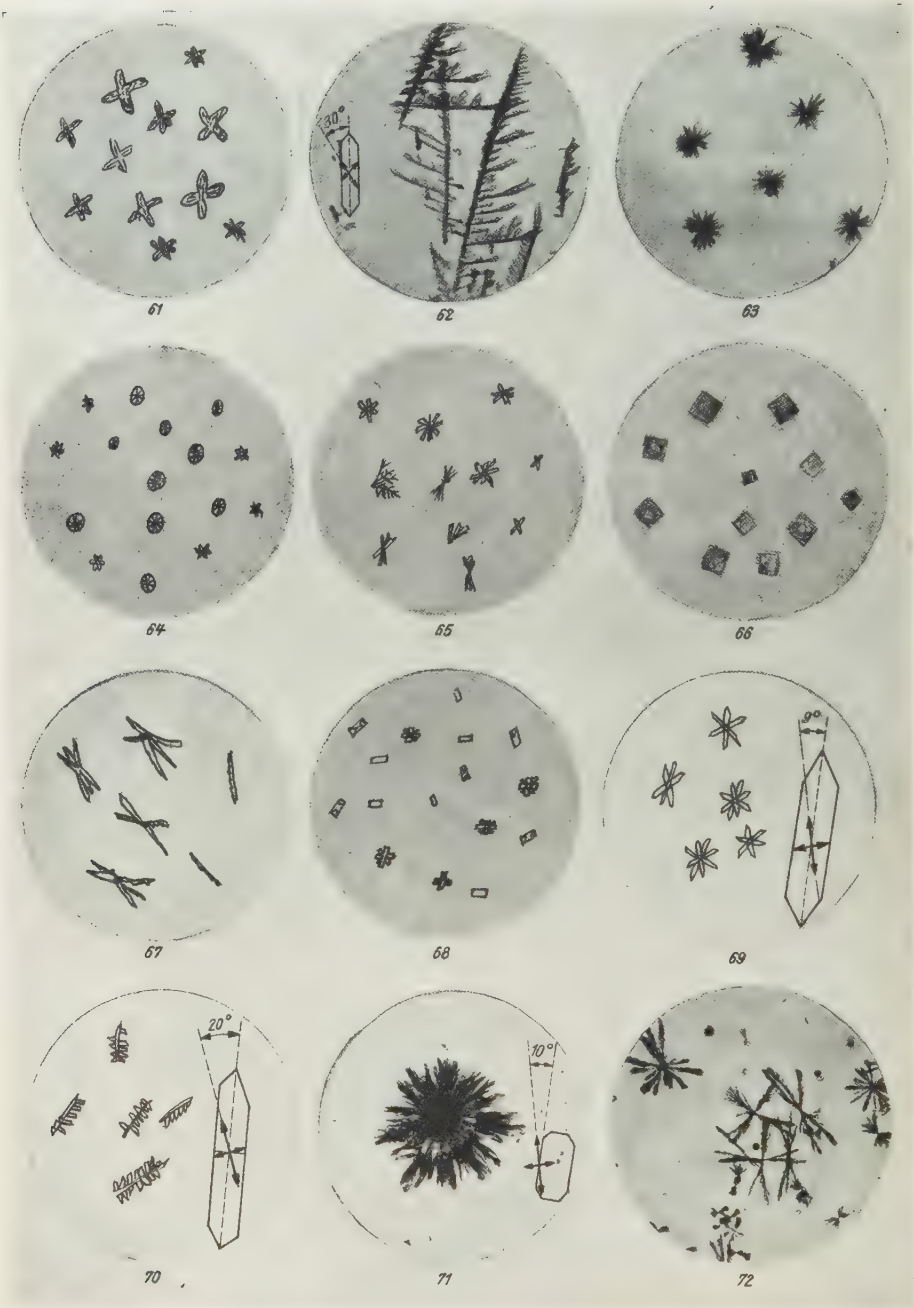

Table VI

Test Forms with $IrCl_4$: Fig. 61. Beta Eucaine, Fig. 62. Cocaine, Fig. 63. Cinchonidine, Fig. 64. Heroine, Fig. 65. Narcotine, Fig. 66. Papaverine, Fig. 67. Brucine, Fig. 68. Strychnine. *Test Forms with Na_2OsCl_6 Reagent:* Fig. 69. Beta Eucaine, Fig. 70. Cocaine, Fig. 71. Cinchonine, Fig. 72. Cinchonidine.

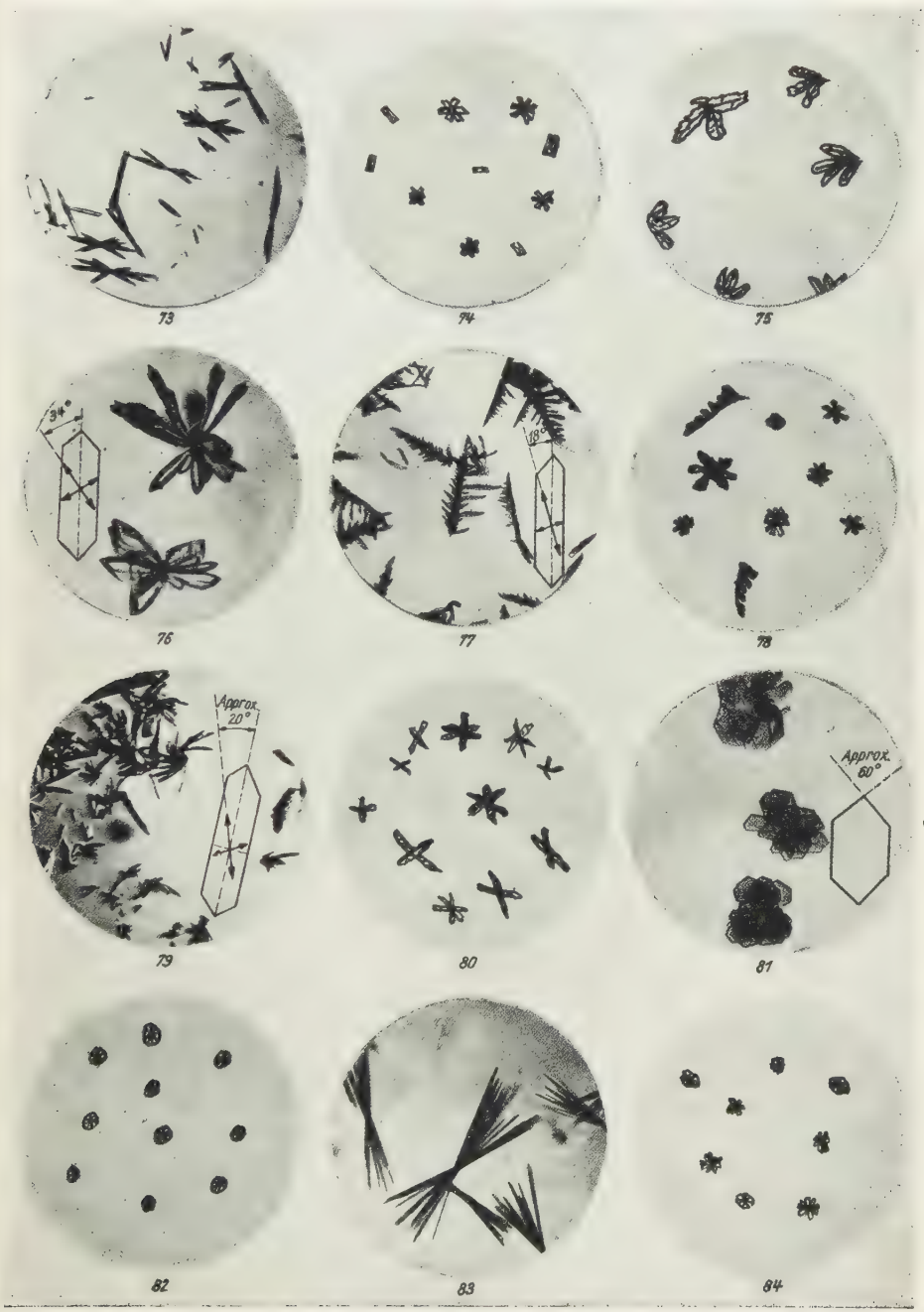

Table VII

Test Forms with Na_2OsCl_6 Reagent: Fig. 73. Brucine, Fig. 74. Strychnine, Fig. 75. Caffeine. *Test Forms with H_2PtBr_6 Reagent:* Fig. 76. Beta Eucaine, Fig. 77. Cocaine, Fig. 78. Novocaine, Fig. 79. Cinchonine, Fig. 80. Cinchonidine, Fig. 81. Quinine + HSO_4^-, Fig. 82. Codeine, Fig. 83. Dionine, Fig. 84. Heroine.

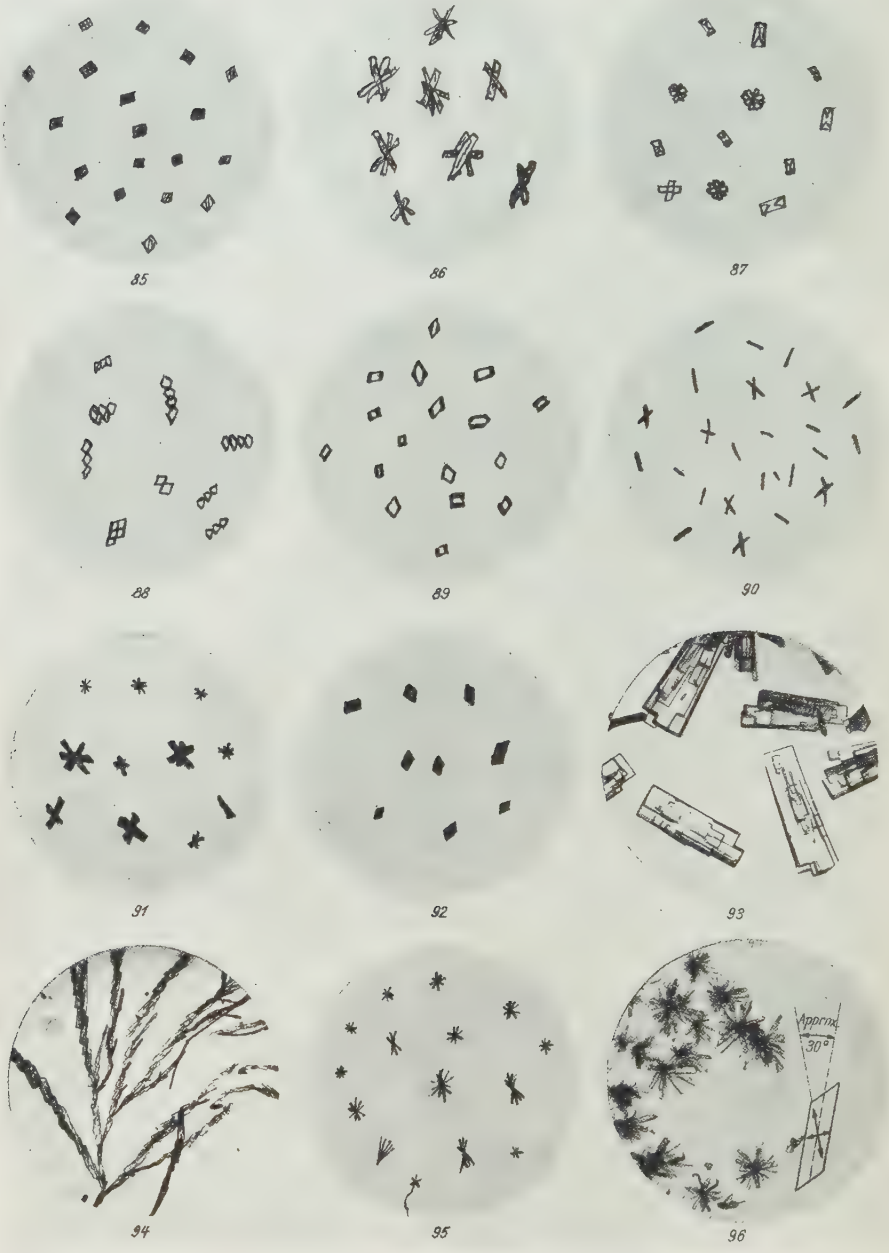

Table VIII

Test Forms with H_2PtBr_6: Fig. 85. Papaverine, Fig. 86. Brucine, Fig. 87. Strychnine, Fig. 88. Caffeine, Fig. 89. Nicotine. *Test Forms with K_2PtI_6 Reagent:* Fig. 90. Cinchonidine, Fig. 91. Caffeine, Fig. 92. Nicotine. *Test Form with $CdCl_2$ Reagent:* Fig. 93. Heroine. *Test Form with $CdBr_2$ Reagent:* Fig. 94. Novocaine. *Test Forms with CdI_2 Reagent:* Fig. 95. Morphine, Fig. 96. Codeine.

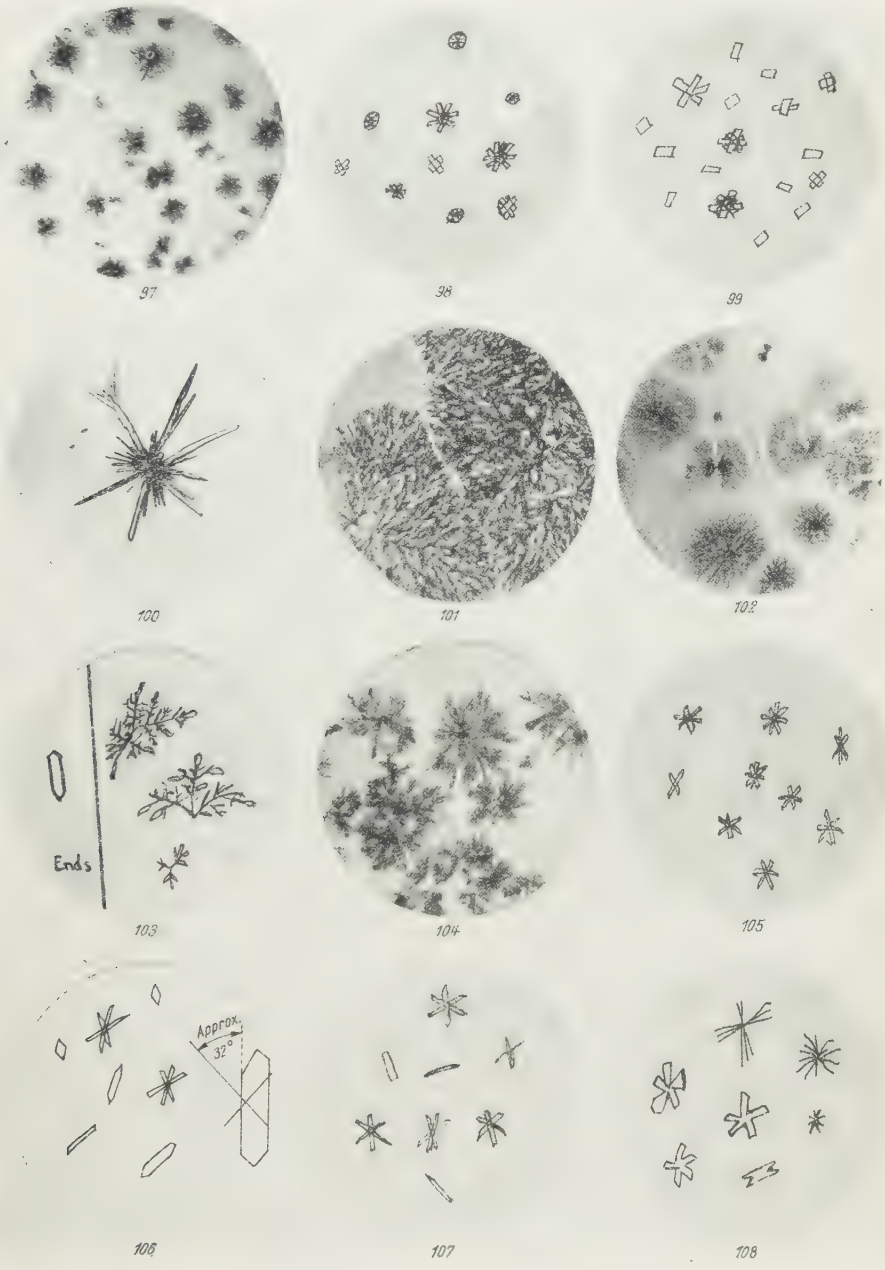

Table IX

Test Forms with CdI_2 Reagent: Fig. 97. Papaverine, Fig. 98. Brucine, Fig. 99. Strychnine. *Test Form with $Cd(NO_3)_2 \cdot NH_4SCN$ Reagent:* Fig. 100. Nicotine. *Test Forms with K_2HgBr_4 Reagent:* Fig. 101. Codeine, Fig. 102. Morphine, Fig. 103. Brucine, Fig. 104. Nicotine, Fig. 105. Strychnine, Fig. 106. Beta Eucaine, Fig. 107. Dionine. *Test Form with $K_2Hg(SCN)_4$ Reagent:* Fig. 108. Brucine.

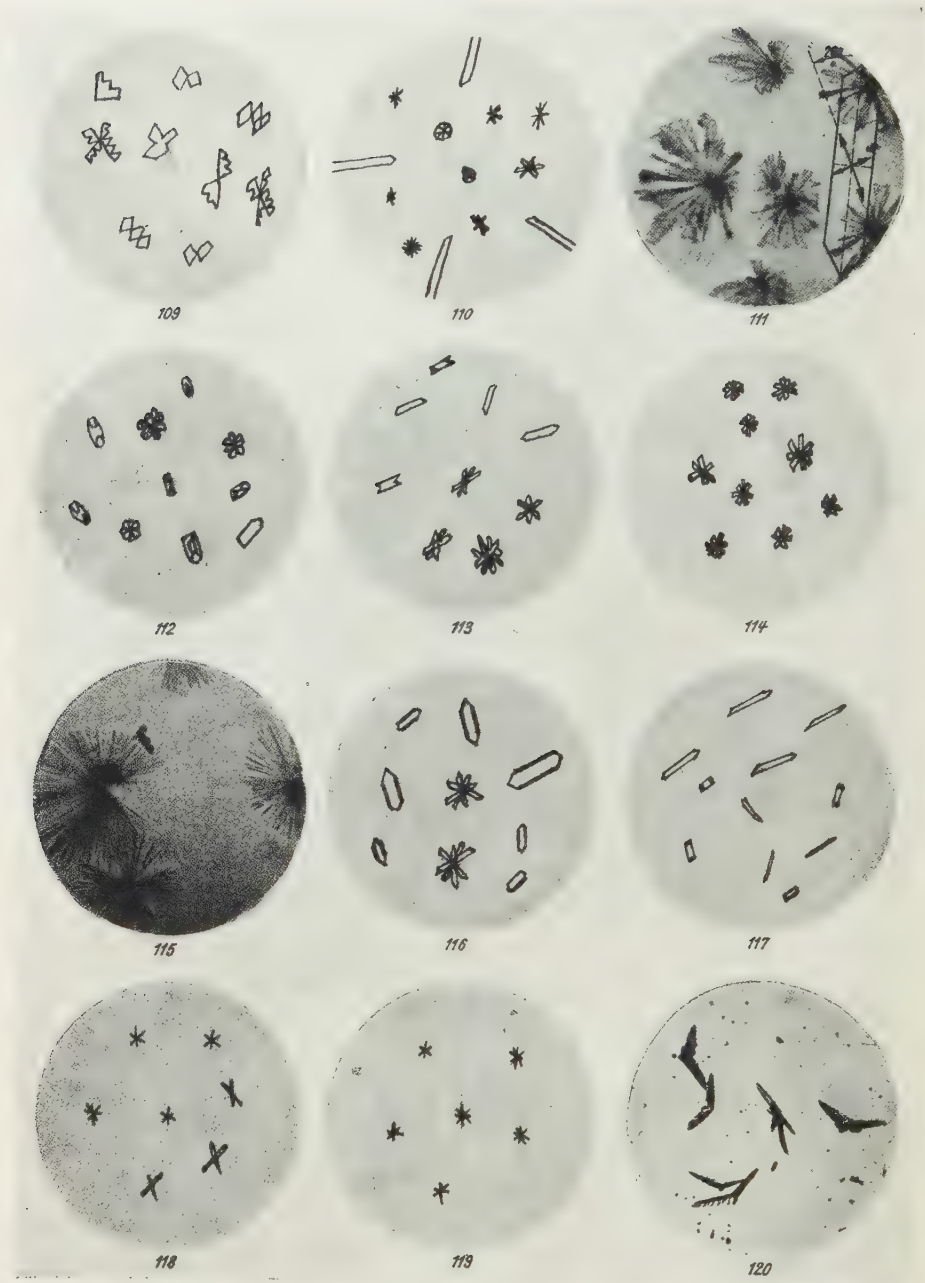

Table X

Test Form with $K_2Hg(SCN)_4$ Reagent: Fig. 109. Strychnine. *Test Form with Potassium-Thallic Iodide Reagent:* Fig. 110. Strychnine. *Test Forms with H_2SnCl_6:* Fig. 111. Beta Eucaine, Fig. 112. Cocaine, Fig. 113. Brucine, Fig. 114. Strychnine. *Test Form with $HSbCl_4$:* Fig. 115. Strychnine. *Test Forms with $MnSO_4 + NH_4SCN$ Reagent:* Fig. 116. Brucine, Fig. 117. Nicotine. *Test Forms with $RhCl_3$:* Fig. 118. Brucine. Fig. 119. Strychnine. *Test Form with $RuCl_3$:* Fig. 120. Cocaine.

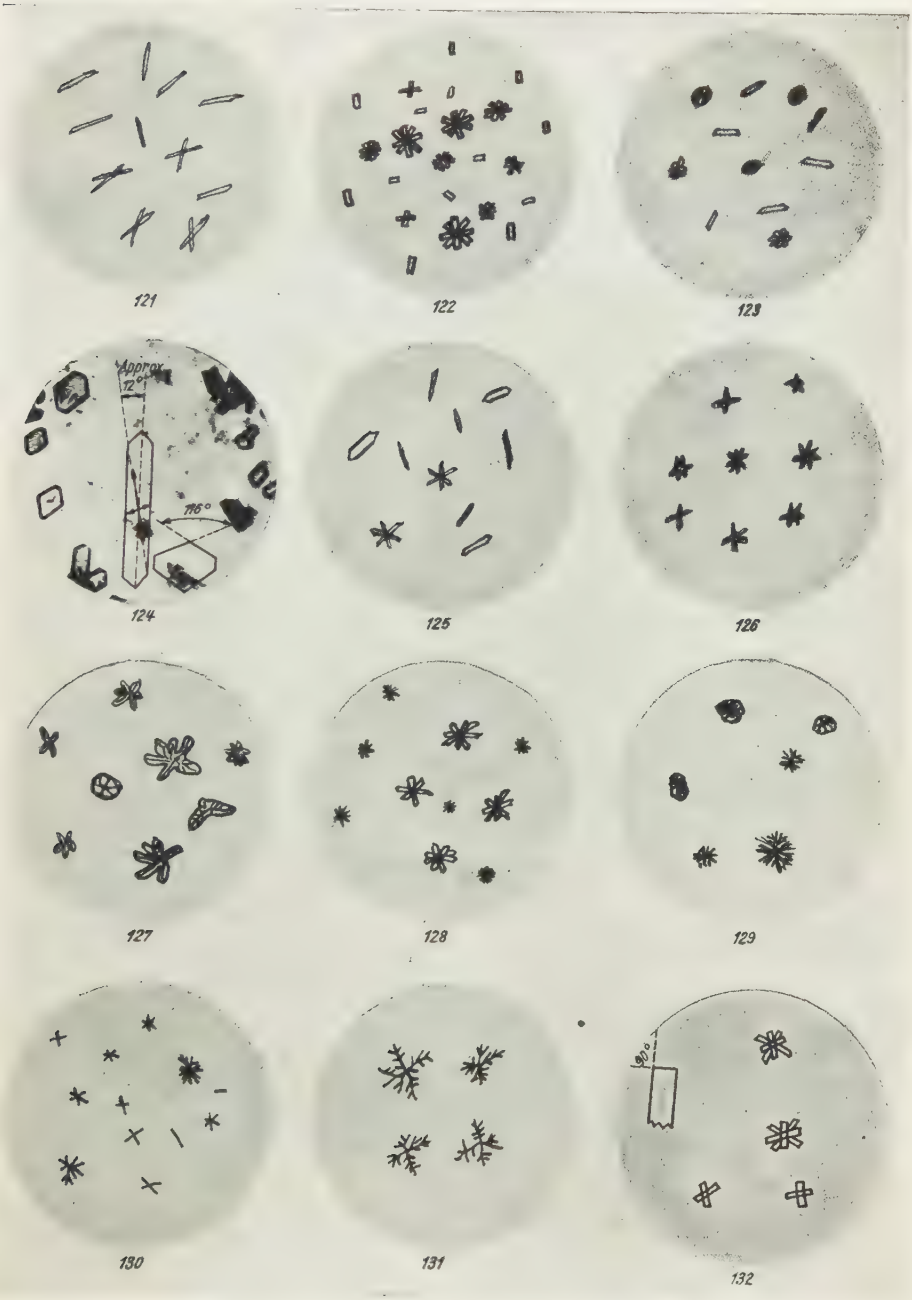

Table XI

Test Forms with $RuCl_3$: Fig. 121. Brucine, Fig. 122. Strychnine. *Test Forms with $Co(NO_3)_2$ + NH_4SCN Reagent:* Fig. 123. Brucine, Fig. 124. Nicotine. *Test Forms with $NiSO_4$ + NH_4SCN Reagent:* Fig. 125. Brucine, Fig. 126. Nicotine. *Test Forms with K_2PdBr_4 Reagent:* Fig. 127. Beta Eucaine, Fig. 128. Brucine, Fig. 129. Strychnine, Fig. 130. Caffeine. *Test Forms with Na_2SnI Reagent:* Fig. 131. Cocaine, Fig. 132. Novocaine.

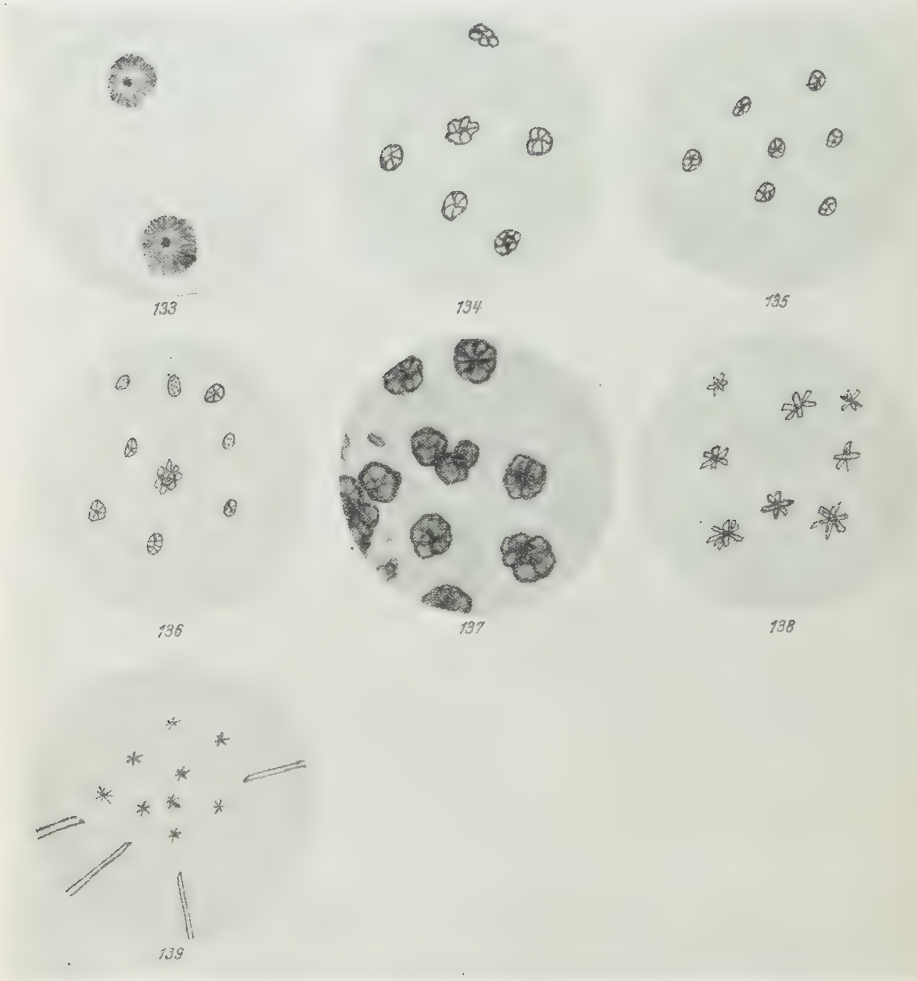

Table XII

Test Forms with Na_2SnI_4 Reagent: Fig. 133. Cinchonidine, Fig. 134. Codeine, Fig. 135. Dionine, Fig. 136. Heroine, Fig. 137. Morphine, Fig. 138. Brucine, Fig. 139. Strychnine.

From the Analytical Laboratories of Fordham University, New York, N. Y.

Studies on the Application of Salts of Complex Cations to the Microscopic Detection of Anions

By

W. A. Hynes and L. K. Yanowski

(Received, May 17, 1939)

IX

Monoaquopentamminocobaltic Chloride (Roseocobaltic Chloride)

The monoaquopentamminocobaltic chloride, or roseocobaltic chloride, $[Co(NH_3)_5(H_2O)]Cl_3$, used in this study was purchased on the open market. This product, on analysis, checked well with the theoretical values for chlorine and nitrogen.[1]

Owing to the transition of the roseo to the purpureo salt when in solution, the reagent was added as a solid at one side of the test drop.[2] The test substances were identical with those previously reported.[3]

Experimental Part

The crystals of reaction products were checked against those of the test substances and reagent alone, and only those forms which differed characteristically from those of the reagent or test substances were considered.

An amount of the reagent approximating a pin-head in size was added to a drop of distilled water, and the mixture allowed to crystallize spontaneously. The form assumed is shown in Fig. 1.

Oxalate ion: A drop of solution containing approximately 1% of the anion (15,2 mg. of $Na_2C_2O_4$/ml.) was added to the reagent and immediately formed small needles tending to clump as shown in Fig. 2.

[1] We wish to thank Mr. *J. Alicino* for the micro Dumas (N calc., 26,09%; found, 26,09%) and for the determination of Cl microgravimetrically as AgCl (calc., 39,62%; found, 39,56%).

[2] *E. M. Chamot* and *C. W. Mason*, Handbook of Chemical Microscopy, Vol. II, p. 30. New York 1931.

[3] *W. A. Hynes* and *L. K. Yanowski*, Mikrochemie **23**, 1, 143, 280 (1937/38); **24**, 1 (1938); **25**, 57, 61 (1938); **26**, 245 (1939).

Dithionate ion: When acted upon by the reagent, a drop of solution containing approximately 1% of the anion (15,1 mg. of $Na_2S_2O_6 \cdot 2\ H_2O$/ml.) immediately formed crystals as shown in Fig. 3.

Sulfosalicylate ion: A drop of solution containing 10 mg./ml. of $C_6H_3(COOH)(OH)(SO_3H)$ on reacting with the reagent immediately formed long, rapidly growing needles (cf. Fig. 4).

Ferricyanide ion: A drop of solution containing approximately 0,5% of anion (6,75 mg. of $K_3Fe(CN)_6$/ml.) reacted immediately to furnish rods as shown in Fig. 5.

Ferrocyanide ion: A drop of the solution containing approximately 0,2% of anion (4 mg. of $K_4Fe(CN)_6 \cdot 3\ H_2O$/ml.) immediately formed long fine needles together with amorphous masses (cf. Fig. 6).

Fluosilicate ion: A drop of the saturated test solution, containing approximately 0,05% of anion (0,6 mg. of Na_2SiF_6/ml.) reacted in 7 minutes to form small tablets as shown in Fig. 7.

Phosphomolybdate ion: A drop of the solution containing approximately 1% of anion (10,4 mg. of $Na_3PO_4 \cdot 12\ MoO_3$/ml.) reacted immediately to form very small pointed rods as shown in Fig. 8.

Non-characteristic precipitates were obtained with naphthionic and tartaric acids and with alkali metal salts of the following anions: benzoate, bifluoride, chromate, cobaltinitrite, iodate, orthovanadate, persulfate, silicate, tetraborate and thiosulfate.

Turbidities of varying densities, which did not become crystalline within the specified time limit (10 minutes), were obtained with phosphomolybdic, phosphotungstic and silicotungstic acids, dipicrylamine, and with alkali metal salts of the following anions: biniodate, metaphosphate, metavanadate, molybdate, paratungstate, phosphotungstate, pyroantimonate, sulfite, tellurate, tungstate and xanthate.

No reactions were obtained with benzoic, boric, citric, formic, maleic, malonic, oxalic, salicylic, succinic, sulfanilic and uric acids, and with alkali metal salts of the following anions: acetate, azide, bicarbonate, bisulfate, bisulfite, bitartrate, borotartrate, bromate, bromide, carbonate, chlorate, citrate, dichromate, fluoride, formate, hypophosphite, iodide, metaborate, nitrate, nitrite, nitroprusside, orthoarsenate, orthoarsenite, secondary orthophosphate, perchlorate, permanganate, pyrophosphate, salicylate, selenate, selenite, succinate, sulfate, tartrate, tellurite and thiocyanate.

We recommend the crystals formed upon reaction of the roseo chloride with oxalate, sulfosalicylate, dithionate and ferricyanide for detection of these anions.

Summary

Roseocobaltic chloride was found to furnish characteristic crystalline reaction products with oxalates, sulfosalicylic acid, dithionates, ferri-

Fig. 1. Roseocobaltic chloride alone, 100×

Fig. 2. Oxalate, 100×

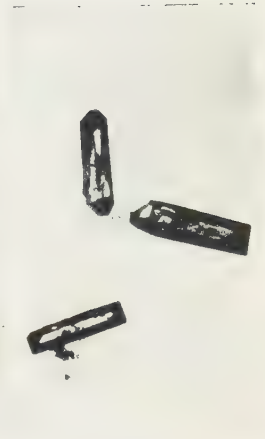

Fig. 3. Dithionate, 100×

Fig. 4. Sulfosalicylate, 100×

Fig. 5. Ferricyanide, 100×

Fig. 6. Ferrocyanide, 100×

Fig. 7. Fluosilicate, 100×

Fig. 8. Phosphomolybdate, 440×

Fig. 1—8. Tests with Monoaquopentamminocobaltic Chloride

and ferrocyanides, silicofluorides and phosphomolybdates. Of these, only the first four reaction products are recommended for identification of the corresponding anions.

Zusammenfassung.

Aquo-pentammino-cobaltichlorid gibt mit Dithionat, Ferricyanid, Oxalat und Sulfosalicylat kristallisierte Reaktionsprodukte, die für den Nachweis dieser Ionen geeignet sind.

Résumé *(L).*

L'aquo-pentammino-cobaltichlorure, forme des dithionates, ferri-cyanures, oxalates et sulfosalicylates cristallins qui conviennent pour la recherche de ces ions.

Contribution from the Chemical Laboratories of New York University

Quantitative Microdeterminations with the Use of Ordinary Analytical Balances

By

A. A. Benedetti-Pichler and R. A. Paulson

(Received, May 29, 1939)

The question of the minimum size of sample required for attaining a specified precision of the analytical result when performing microdeterminations with the use of ordinary analytical balances has been treated mathematically in a previous paper.[1] The usefulness of the deductions was tested by *Niederl, Niederl,* and *Nagel*[2] by applying them to the practice of quantitative microdeterminations in the field of organic elementary analysis. The following report deals essentially with microdeterminations of inorganic substances. Only four different types of determinations were tried, but in each instance a fairly large number of experiments was performed so as to obtain a reliable figure for the average deviation of the results.

Selection of Balances

The balances were chosen more or less at random from analytical balances of American manufacture which had been used by students for five and more years. Following the principles developed in previous publications,[1, 3] the precision of these balances was determined for a load of 10 g. on each pan. The results are compiled in table I. It may be pointed out that all of the balances belong to the same simple type which is generally used in the United States for students' work and which is listed to-day at approximately 65 dollars. The balances are of a rather

---

[1] *A. A. Benedetti-Pichler,* Ind. Engin. Chem., Analyt. Ed. **11**, 226 (1939); see also Mikrochemie **25**, 390 (1939), where the last sentence of page 390 should read: „Falls ω in Zehntelmilligrammen eingesetzt wird, errechnet sich das Volumen von E in Kubikmillimetern."

[2] *J. B. Niederl, V. Niederl, R. H. Nagel,* and *A. A. Benedetti-Pichler,* Ind. Engin. Chem., Analyt. Ed. **11**, 412 (1939).

[3] *A. A. Benedetti-Pichler,* Ind. Engin. Chem., Analyt. Ed. **8**, 373 (1936); see also Mikrochemie **20**, 337 (1936).

light construction: the knife edges of agate are swaged or cemented into the beam (Fig. 1). The rider scale is placed along the un-notched top edge of the beam, and the divisions usually appear in white against a black background. The arresting mechanism is of the simplest type: rotation of a milled head in the front of the base plate releases the beam and the stirrups, and a push button, usually situated close to the milled head, releases the pans. The latter are suspended directly from the hooks of the stirrups and, as a rule, no special provisions are made in the construction of the stirrups which would reduce the influence of the distribution of masses on the pans upon the position of the agate plates of the terminal bearings.

Table I. Data on Students' Balances.

No.	Manufacturer	In use since	Average deviation, October 1938, ± gamma
1	A	1934	28
2	B	1925	15
3	A	1934	19
4	C	1925	38[1]
5	D	1926	60

There is no record available of the life history of the five balances chosen. They assuredly were not given special consideration when in use,

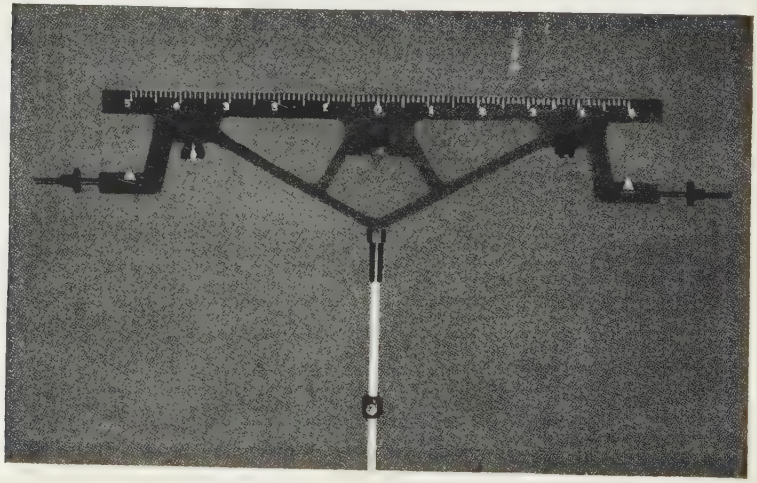

Fig. 1. Typical beam of inexpensive analytical balances made in the United States.

and, being situated on a not too rigid table in a room with considerable traffic, they certainly suffered many serious jolts and jars in addition to the rather severe continuous vibrations present in the building. Repairs or adjustments may have been performed occasionally, since it is custo-

[1] Originally the average deviation of this balance was equal to ± 26 gamma; see text.

mary to have a mechanic go over the balances during the summer vacation. Considering the construction of the beam, one may easily expect that on some of the balances the knife edges are no longer properly aligned. Fortunately, however, faults of a balance which might have serious consequences in determinations of absolute mass do not matter in most analytical work.

Riders weighing 5 mg. were used with all of the five balances. Balance No. 1 is the same as was used by *Niederl* and *Nagel*.[1] Balances No. 2 and No. 4 were employed in the work reported below. Balance No. 4 originally showed an average deviation of ± 26 gamma for a single weighing and a sensitivity of 26 units of the pointer scale per milligram.[2] Since the balance swung rather rapidly and we were accustomed to adjust the sensitivity of our balances to 5 or 6 divisons per milligram, we expected a gain in precision by a similar adjustment of balance No. 4. The average deviation of a single weighing increased, however, to the value given in table I when the sensitivity was bettered to 67 units of the pointer scale per milligram. It was finally decided to retain this adjustment of balance No. 4, since it seemed desirable to try microdeterminations wich an instrument of rather poor precision of close to 40 or 50 gammas.

Determination of Sodium in Sodium Oxalate

Sodium oxalate of tested purity as suggested by *Sørensen* for the standardization of potassium permanganate solutions was converted to sodium sulfate by ignition with sulfuric acid. The oxalate was weighed out into small platinum crucibles of the form recommended by *Pregl*[3], and each sample was treated with 1 cmm. conc. sulfuric acid for each milligram of sample. Loss of material because of creeping during the removal of the excess acid was prevented by heating the crucibles on a copper plate of 24 cm. length, 3 cm. width, and 5 mm. thickness which was provided with three circular holes. These were bored in a row along the middle line of the copper plate, 2 cm. apart, and starting at a distance of 4 cm. from one end of the plate. The holes were bored in a slightly conical fashion and carefully polished so as to fit snuggly around the walls of the platinum crucibles. The diameter of the holes was selected so that the crucibles were held by the plate halfway between the bottom and top. The copper plate was laid across a ring support and the crucibles were placed in the holes and covered with their lids. A short thermometer was laid on the metal close to the crucibles and the far end of the plate was heated with a Tirrill burner so that the

[1] See footnote 2, p. 339.

[2] See footnote 1, p. 339.

[3] *F. Pregl (H. Roth)*, Die quantitative organische Mikroanalyse, 4th ed., p. 168. Berlin 1935.

thermometer indicated a temperature of 250° C. within from 12 to 15 minutes. Sulfur trioxide fumes begun to appear at 180°; when 250° was reached, the sulfuric acid was usually expelled, otherwise the latter temperature was held until the liberation of fumes ceased. The method of heating, which is based on a principle[1] much utilized in microanalysis, efficiently prevents creeping even when relatively large samples are ashed.

When the fumes of sulfur trioxide had been expelled, the crucibles were heated in a quartz evaporating dish for 5 minutes at the full heat of a Tirrill burner. The crucibles were then opened and placed for 15 minutes under a bell jar close to a dish with ammonia so as to change any bisulfate formed to sulfate. Finally the crucibles were heated as before, first on the copper bar and then in the evaporating dish. The treatment with ammonia, followed by ignition, was repeated to constant weight. Working with samples of 16 to 18 mg., several repetitions of this treatment were required and, as a result, three and one-half hours were required for the simultaneous performance of two such determinations. Nevertheless, the residues of determinations 10 and 12 (table II) reacted slightly acid toward litmus paper, which indicates the presence of some bisulfate.

Table II. Determination of Sodium

$P = 34{,}34\%$ Na in sodium oxalate.
$f = 0{,}3238$, chemical factor. $0{,}5\,P < 100\,f < P$ (see footnote 1, p. 339).

With use of balance No. 2:
Minimum weight of sample calculated, $S = 6{,}0$ mg.

No.	$Na_2C_2O_4$ taken mg.	Na_2SO_4 obtained mg.	Na found %	
1	10,56	11,18	34,26	Arithmetical mean of the
2	8,66	9,18	34,32	series = 34,38% Na
3	10,28	10,90	34,34	Average deviation of a single
4	5,70	6,03	34,25	determination from the mean,
5	7,06	7,45	34,17	$a_s = \pm$ 0,08% Na
6	6,14	6,54	34,46	Relative average deviation of
7	7,38	7,80	34,22	a single determination from
8	6,12	6,50	34,38	the mean,
9	6,18	6,52	34,15	$a'_s = \pm$ 2,4‰

With use of balance No. 4:
Minimum weight of sample calculated, $S = 15{,}2$ mg.

10	18,33	19,54	34,50	
11	16,58	17,57	34,30	Mean of series = 34,35% Na
12	17,11	18,16	34,37	$a_s = \pm$ 0,08% Na
13	18,17	19,19	34,19	$a_s' = \pm$ 2,4‰
14	16,16	17,16	34,38	

[1] *W. Lenz*, Z. analyt. Chem. **52**, 90 (1913).

In the final experiments, creeping occurred only in one instance (determination 8 of table II). Aside from being the cause of mechanical losses of substance, creeping may also introduce positive deviations as was recognized in earlier experiments. This is so because, with the recommended procedure of ignition, sodium sulfate clinging to the upper part of the crucible walls tenaciously retains sulfur trioxide. Whenever creeping occurred, it could be demonstrated that the residue contained unusually large quantities of bisulfate.

Determination of Aluminium in Alum

The aluminium was weighed as 8-hydroxyquinolate. The procedure has been described in detail in an earlier publication.[1] Slight changes were made in order to facilitate the application of the method to the larger quantities of aluminium required when working with analytical balances.

To increase the active filtering surface of the asbestos mat, a ball of platinum wire about 2 mm. in diameter, which was prepared by wadding 30 cm. of wire (0,1 mm. diameter), was introduced into the filterstick as support for the asbestos filling. The sample was weighed out into a microbeaker of 10 ml. capacity (16 mm. diameter and 6 to 7 cm. height). It was dissolved in 0.2 M hydrochloric acid using 0,15 ml. of this acid for each milligram of alum. Then 0,03 ml. of the oxine reagent was added for each milligram of alum present. The beaker was placed on a steam bath, and 2 M ammonium acetate solution was added slowly, dropwise with mixing after each addition, until a permanent turbidity formed. Now the mixture was heated on the steam bath until the precipitate appeared distinctly crystalline, which took approximately one minute, and then more of the ammonium acetate solution was added dropwise until the precipitation appeared complete; usually 1 or 2 drops of the reagent were sufficient to reach this state. Excess of the ammonium acetate solution was then added, 0,08 ml. being used for each milligram of alum. The precipitate and the mother liquor were allowed to stand for 10 minutes on the steam bath, after which the hot supernatant solution was drawn off through the filterstick. The precipitate was sucked dry and washed with hot water, using 0,25 ml. per milligram of alum as total amount of wash liquid. It was then dried at 140° C. in a current of air;[1] even with the relatively large amounts of hydroxyquinolate, 5 minutes of drying proved to be sufficient. The results are given in table III.

The necessity of a strict adherence to the prescribed conditions of concentration is illustrated by 3 experiments with 16 to 18 milligrams of alum, in which only 0,5 ml. excess of 2 M ammonium acetate solution was

[1] *A. A. Benedetti-Pichler*, Mikrochemie, *Pregl*-Festschrift, p. 6 (1929).

added. Distinctly low results (10,66, 10,64, and 10,71% Al_2O_3) were obtained which were obviously caused by the lack of acetate and the consequently increased hydrogen ion concentration.

Table III. Determination of Aluminium

$P = 10{,}74\%$ Al_2O_3 in potassium alum.
$f = 0{,}1112$. $P < 100\,f < 2\,P$ (see footnote 1, p. 339).

With the use of balance No. 2:
Minimum weight of sample calculated, $S = 6{,}2$ mg.

No.	Alum taken mg.	8-Hydroxyquinolate obtained mg.	Al_2O_3 found %	
1	6,20	6,00	10,74	
2	6,74	6,56	10,80	Arithmetical mean of the
3	7,40	7,14	10,70	series = 10,75% Al_2O_3
4	7,64	7,38	10,72	$a_s = \pm 0{,}04\%$ Al_2O_3
5	8,50	8,26	10,78	$a_s' = \pm 3{,}7‰$
6	6,22	5,98	10,72	
7	7,04	6,86	10,81	

With use of balance No. 4:
Minimum weight of sample calculated, $S = 15{,}8$ mg.

8	17,51	16,78	10,64	
9	16,50	15,96	10,73	Mean of series = 10,71% Al_2O_3
10	17,79	17,27	10,76	$a_s = \pm 0{,}03\%$ Al_2O_3
11	17,50	16,89	10,71	$a_s' = \pm 2{,}8‰$
12	16,22	15,69	10,73	

Determination of Calcium

The calcium oxide of Iceland spar was determined by precipitating and weighing calcium oxalate monohydrate. A detailed description of the procedure has been given in a former publication.[1] Balance No. 4 of lesser precision was used and 16 to 18 mg. of Iceland spar were weighed out into a microbeaker of 10 ml. capacity. The sample in the beaker was covered with 1 ml. distilled water and then concentrated hydrochloric acid was added dropwise until solution was complete. The dissolved carbon dioxide was finally removed by heating on the steam bath. The solution of the sample was then removed from the steam bath and treated with a 3% solution of oxalic acid, using 0,15 ml. of it for each milligram of Iceland spar. One drop of alcoholic solution of methyl red was added and then 2 M ammonia solution was introduced dropwise until the first turbidity appeared. The mixture was now heated on the steam bath until the turbidity dissolved and more 2 M ammonia was added dropwise to the

[1] *A. A. Benedetti-Pichler*, Z. analyt. Chem. **64**, 420 (1924).

hot solution until it seemed that one or two drops more would cause a permanent turbidity. The precipitation was then completed on the steam bath by adding 1 M ammonia dropwise, with mixing, until the color of the solution changed to yellow. The precipitate was allowed to stand under cover for one hour. The solution was then drawn off through a filter stick and, since the precipitate tended to clog the asbestos mat, only the clear supernatant liquid was removed. The precipitate was washed four times, using 0.75 ml. of cold water each time, but it was not drawn up into the filterstick until after the last washing. The precipitate was finally dried for 10 minutes at 100° to 105° C. in a current of air.[1] The results are given in table IV.

Table IV. Determination of Calcium

$P = 56{,}03\%$ CaO in calcium carbonate.
$f = 0{,}3838$. $0{,}5\,P < 100\,f < P$ (see footnote 1, p. 339).
With use of balance No. 4:
Minimum weight of sample calculated, $S = 15{,}2$ mg.

No.	Iceland spar taken mg.	$CaC_2O_4 \cdot H_2O$ obtained mg.	CaO found %	
1	16,98	24,68	55,77	
2	15,01	22,02	56,30	
3	17,20	24,98	55,75	Arithmetical mean of the
4	17,79	25,91	55,89	series = 56,00% CaO
5	16,83	24,53	55,94	$a_s = \pm$ 0,20% CaO
6	15,95	23,39	56,28	$a_s' = \pm$ 3,6‰
7	16,67	24,25	55,84	
8	16,61	24,32	56,19	

Determination of Magnesium

The magnesium oxide of freshly crystallized magnesium sulfate heptahydrate was determined by precipitating and weighing magnesium-ammonium phosphate hexahydrate; the exact procedure may be found in a preceding publication.[2] Balance No. 4 of lesser precision was used and 16 to 17 milligrams of the magnesium sulfate were weighed out into a microbeaker of 10 ml. capacity. For each milligram of sample 0,2 ml. of a solution containing thirty grams of ammonium chloride per liter was added. The contents of the beaker were then heated nearly to boiling temperature and, immediately after removal from the steam bath, treated with ammonia and phosphate solution. For each milligram of sample 0,02 ml. of 10% ammonia and 0,02 ml. of a 10% solution of secondary

[1] See footnote 1, p. 343.

[2] *A. A. Benedetti-Pichler* and *Frank Schneider*, Mikrochemie, *Emich*-Festschrift, p. 8 (1930).

sodium phosphate dodekahydrate were used. The contents of the beaker were mixed well and allowed to stand for at least 6 hours. Then the supernatant solution was drawn off the crystalline precipitate with the aid of an asbestos filterstick, and the precipitate was washed four times with 1% ammonia using 1 ml. each time. Filtration and washing could be accomplished more easily when the precipitate was allowed to settle and just the clear liquid was drawn off. The precipitate was sucked dry after the last washing with ammonia. Beaker and filterstick were then rinsed with 1 ml. of ethyl alcohol. The alcohol was not completely sucked off, the suction being interrupted while there was still a small amount of alcohol left in the beaker. The precipitate was then dried in a current of air which had been passed through a drying tower containing calcium chloride hexahydrate. Ten minutes of drying gave constant weight. The results are given in table V.

Table V. Determination of Magnesium

$P = 16{,}36\%$ MgO in magnesium sulfate heptahydrate.
$f = 0{,}1643$. $P < 100\,f < 2\,P$ (see footnote 1, p. 339).
With use of balance No. 4:
Minimum weight of sample calculated, $S = 15{,}2$ mg.

No.	$MgSO_4 \cdot 7\,H_2O$ taken mg.	$MgNH_4PO_4 \cdot 6\,H_2O$ obtained mg.	MgO found %	
1	16,19	16,11	16,34	
2	16,50	16,33	16,25	Arithmetical mean of the
3	16,41	16,24	16,25	series = 16,34% MgO
4	16,06	16,14	16,50	$a_s = \pm 0{,}07\%$ MgO
5	15,87	15,85	16,40	$a_s' = \pm 4{,}1‰$
6	16,94	16,81	16,29	
7	15,69	15,62	16,35	

Summary

The predictions of a preceding paper dealing with the minimum size of sample as a function of the precision of the balance used were put to a practical test. Students' balances were employed in the experiments, one with an average deviation of the single weighing of $\pm$ 0,015 mg. and another of $\pm$ 0,038 mg. Series of determinations on samples of 6 to 8 mg. and 16 to 18 mg. showed average deviations of the results from 2,4 to 4,1‰. The largest deviation actually obtained in these series amounted to 10‰ of the result, while 20‰ are foreseen in the derivation of the equations for the calculation of the minimum mass of sample. The chances for the occurrence of a deviation of 20‰ are, however, small enough so that its observation in such a small number as 41 determinations must not be expected.

Zusammenfassung.

Eine vorangehende Arbeit behandelte den Zusammenhang zwischen der Mindestmenge der Probe und der Präzision der benützten Waage von einem theoretischen Gesichtspunkte aus. Die gewonnenen Formeln wurden nun einer praktischen Prüfung unterzogen. Analytische Waagen, die zum Teil seit Jahren von Studenten benützt worden waren, wurden für die Ausführung der Wägungen herangezogen. Eine dieser Waagen zeigte eine Durchschnittsabweichung der einzelnen Wägung von $\pm$ 0,015 mg, die Präzision der zweiten Waage wurde zu $\pm$ 0,038 mg bestimmt. Reihen von Bestimmungen mit Proben von 6 bis 8 mg bzw. 16 bis 18 mg Gewicht zeigten Durchschnittsabweichungen der Resultate von 2,4 bis 4,1‰. Die größte beobachtete Abweichung betrug 10‰ des betreffenden Resultates, während die theoretische Ableitung das Vorkommen eines Maximalfehlers von 20‰ vorsieht. Die Wahrscheinlichkeit des Auftretens der maximalen Abweichung ist jedoch so gering, daß es nicht überraschen kann, daß diese Abweichung in der verhältnismäßig kleinen Zahl von Bestimmungen nicht beobachtet wurde.

Die verwendeten analytischen Waagen sind billige Waagen für Unterrichtszwecke, wie sie in den Vereinigten Staaten erzeugt werden. Sie sind von leichter Konstruktion und die Achatschneiden sind in den Balken eingezogen. Die Reiterlineale sind ohne Kerbungen ausgeführt. Da die Verbindung zwischen den Schalen und den Endschneiden infolge Fehlens eines Zwischengehänges eine gewisse Starrheit aufweist, ist die Art der Verteilung der Massen auf der Waagschale von einigem Einfluß auf das Wägungsergebnis.

Résumé *(W).*

Un travail antérieur a traité d'un point de vue théorique le rapport existant entre la quantité minima d'une prise d'essai et la précision de la balance utilisée. Les formules établies ont été soumises à un examen pratique. Des balances analytiques qui avaient été employées depuis des années par des étudiants furent réintroduites pour l'exécution des pesées. Une de ces balances montra un écart moyen de pesée de $\pm$ 0,015 mg, la précision de la seconde balance fut estimée à $\pm$ 0,038 mg. Des séries de déterminations avec des essais de 6 à 8 mg, respectivement, de 16 à 18 mg de poids, présentèrent des écarts moyens de 2,4 à 4,1‰. Le plus grand écart que l'on ait observé, se montait à 10‰ du résultat obtenu alors que la théorie prévoit une faute maxima de 20‰. La probabilité de l'apparition d'un écart maximum est si minime qu'il n'y a pas à être surpris si cet écart n'a pas été observé dans le nombre relativement petit des essais exécutés.

Les balances analytiques telles que celles employées aux E. U. sont des balances peu coûteuses pouvant servir à des buts pédagogiques. Elles sont de légère construction et les couteaux d'agate sont placés dans les fléaux. La ligne sur laquelle se place le cavalier est dépourvue d'encoches. Comme la liaison entre les plateaux et les couteaux, par suite du manque d'une pièce intermédiaire, présente une certaine rigidité, la façon de placer les masses sur le plateau a une certaine influence sur le résultat de la pesée.

Buchbesprechungen.[1]

Erna Brennecke: **Schwefelwasserstoff als Reagens in der quantitativen Analyse.** (41. Band der Sammlung „Die chemische Analyse".) Mit 5 Abb. XII und 234 S. Stuttgart: F. Enke. 1939. RM 20,40; geb. RM 22,—.

Das vorliegende Buch stellt den interessanten und, wie vorweggenommen werden soll, vollauf geglückten Versuch dar, das wichtige Tatsachenmaterial über die Sulfidfällungen der Metalle auf Grund einer kritischen Auswahl der Literaturangaben übersichtlich darzustellen, was einem lang empfundenen Bedürfnis der analytischen Chemiker entgegenkommt. Die geschickte Durchführung dieser Aufgabe charakterisiert das Werk als eine sehr nützliche Neuerscheinung des analytisch-chemischen Schrifttums.

Kapitel I bringt das Wissenswerte über Schwefelwasserstoff, Ammonium- und Alkalisulfide als Reagenzien. Das ausgedehnte Kapitel II (168 Seiten) behandelt die Sulfide der einzelnen Metalle nach folgenden Gesichtspunkten: Einfluß der Fällungsbedingungen, Weiterbehandlung des Niederschlages zwecks Überführung in eine geeignete Wägungsform, Auflösbarkeit des Sulfidniederschlages, Abtrennung des Metalles auf Grund des Verhaltens seines Sulfides. Die Reihe der in dieser Art besprochenen Metalle ist: Quecksilber, Silber, Kupfer, Wismut, Cadmium, Blei, Rhenium, Arsen, Antimon, Zinn, Molybdän, Germanium, Platinmetalle und Gold, Zink, Kobalt, Nickel, zwei- und dreiwertiges Eisen, Mangan, Indium, Tallium. Der Abschnitt III enthält allgemeine Angaben über den Reaktionsablauf bei Sulfidfällungen, Gleichgewichtseinstellung, die Fällbarkeit der nicht eingehender behandelten Elemente und schließlich Trennungen mittels Sulfidfällungen bzw. dabei auftretende Störungen. In Kapitel IV wird die praktische Ausführung der Sulfidfällungen ausführlich besprochen, und zwar an Hand ausgewählter Arbeitsvorschriften für die meisten der früher genannten Metalle. In Abschnitt V finden sich Daten über Nachweis und Bestimmung von Schwefelwasserstoff und Sulfidschwefel, während ein kurzes Anhangskapitel über Gleichgewichtskonstanten, Löslichkeitsprodukte, Verhalten der Sulfide der Schwefelwasserstoffgruppe gegenüber Ammoniak und Ammonsulfiden sowie über colorimetrische Bestimmungen, die auf der Verwendung der Sulfidfällung beruhen, handelt.

Die obige eingehende Anführung des Buchinhaltes soll einen Eindruck über den Umfang des behandelten Tatsachenmaterials vermitteln, das sonst nirgends in so ausführlich gesammelter Form anzutreffen ist. Wer sich mit gravimetrischer Mikroanalyse beschäftigt hat, weiß, daß dabei öfters die Sulfid-

[1] Da die Zeitschrift „Mikrochemie vereinigt mit Mikrochimica Acta" vornehmlich zur Veröffentlichung von Originalarbeiten bestimmt und auch für diese eine knappe Darstellung erforderlich ist, um eine möglichst schnelle Publikation zu gewährleisten, können nur solche Bücher besprochen werden, deren Inhalt für die Mikrochemie von Interesse ist.

fällung von Metallen nicht zu umgehen ist. Um so erfreulicher ist es, nunmehr in unserer chemischen Literatur ein Buch zu besitzen, das bei der Herstellung der richtigen Arbeitsbedingungen wertvolle Winke gewähren kann.

Ungefähr die Hälfte der am Schluß des Buches angeführten Schrifttumsangaben beinhaltet Dissertationen, die unter Leitung des verstorbenen Professors der Technischen Hochschule in München *K. Daniel* ausgearbeitet worden sind. Demgemäß ist das Buch auch dem Andenken dieses verdienstvollen Forschers gewidmet. *F. Hecht*-Wien.

Gmelins **Handbuch der anorganischen Chemie.** 8. Aufl. Herausgegeben von der Deutschen Chemischen Gesellschaft. Berlin: Verlag Chemie.

Systemnummer 59: Eisen; Teil F II, Lieferung 1. Mit 7 Abb. 164 S. 1938. RM 26,—.

Der Teil F des *Gmelin*schen Handbuches umfaßt die Nachweis- und Bestimmungsmethoden der Fremdelemente in Eisen und Stahl. Davon hat die Unterabteilung II die eigentlichen Legierungselemente, die sonstigen Elemente und Sonderverfahren zum Gegenstand. Im vorliegenden Heft werden die folgenden Elemente behandelt: Alkalimetalle, Bor, Beryllium, Zirkon und Hafnium, Selen, Tellur, Gallium, Indium, Tallium, Germanium, Rhenium, Quecksilber, Silber, Gold, Platinmetalle, Zinn, Blei, Zink, Cadmium, Uran, Kupfer, Niob und Tantal, Wolfram, Molybdän, Chrom, Vanadin. Vor den analytischen Verfahren werden bei jedem Element auch das Auftreten und die Bindung in Eisen und Stahl besprochen.

Die vorliegende Lieferung beweist, daß das Ziel der Redaktion des *Gmelin*schen Handbuches, den Teil Eisen F zu einer Monographie auszugestalten, die auch als praktisches Laboratoriumsbuch zu Rate gezogen werden kann, bisher erreicht worden ist. Die Art der Darstellung, die viele ausführliche Arbeitsvorschriften umfaßt, berechtigt zu der Erwartung, daß auch die späteren Lieferungen den erwähnten Zweck erfüllen werden.

Systemnummer 68: Platin; Teil A, Lieferung 1. Mit 2 Abb. 145 S. 1938. RM 22,—.

Nach Anführung der geschichtlichen Daten zur Entdeckung und Erforschung des Platins sowie zur Entdeckung der übrigen Platinmetalle behandelt das vorliegende Heft das Vorkommen der Platinmetalle in der Sonne, den Sternen und den Meteoriten. Den größten Teil der Lieferung nimmt naturgemäß der Bericht über das irdische Vorkommen der Platinmetalle ein. Sehr ausführlich werden dabei deren Geochemie und die lagerstättenkundliche Stellung berücksichtigt, so daß der Abschnitt auch für den Vertreter dieser Fächer von großem Wert ist. Der letzte Teil dieses Kapitels, der allein zwei Drittel des Heftes umfaßt, bringt die ausführliche Besprechung der einzelnen Platinmetallagerstätten in den einzelnen Erdteilen, wovon der überwiegende Teil auf das europäische und asiatische Rußland entfällt.

Das Heft stellt inmitten der übrigen Lieferungen des neuen „Gmelin" eine wichtige Bereicherung der anorganischen Literatur dar.

Systemnummer 27: Magnesium; Teil B, Lieferung 4. Mit 16 Abb. 127 S. 1939. RM 25,—.

Die vorliegende Lieferung schließt den Teil B ab. Es werden darin behandelt die Verbindungen von Magnesium mit Lithium-, Natrium- und Kaliumsalzen, ferner die Verbindungen, welche Magnesium und Ammonium, Magnesium und Hydrazonium, Magnesium und Hydroxylammonium,

Magnesium und Rubidium, Magnesium und Beryllium enthalten. Es folgen die technischen Darstellungsverfahren für Magnesiumoxyd und -hydroxyd, Magnesiumcarbonate, Magnesiumchlorid, Magnesiumsulfat. Den Abschluß bilden wirtschaftsstatistische Mitteilungen über die Produktion von Magnesit, Asbest, Talk und Tropfstein sowie verschiedenen Magnesiumsalzen.

Es braucht nicht besonders darauf hingewiesen zu werden, daß auch dieses Heft alle die bewährten Vorzüge der so sorgfältig bearbeiteten Neuauflage des *Gmelin*schen Handbuches aufweist.

Systemnummer 35: Aluminium; Teil A, Lieferung 6. Mit 97 Abb. 224 S. 1939. RM 37,—.

In Fortsetzung der Legierungen des Aluminiums wird eine große Anzahl weiterer Legierungen mit Mangan, Nickel, Kobalt, Eisen, Kupfer, Silber, Gold, ferner mit den Platinmetallen besprochen. Die Darstellung erstreckt sich innerhalb des bezeichneten Rahmens selbstverständlich auch auf diejenigen Legierungen, welche außer den genannten noch weitere Metalle enthalten.

Bewundernswert ist auch hier wiederum die gewohnte Gründlichkeit der Bearbeitung. *F. Hecht*-Wien.

Otto Niezoldi: **Ausgewählte chemische Untersuchungsmethoden für die Stahl- und Eisenindustrie.** 2. verm. u. verb. Aufl. VIII und 175 S. Berlin: Julius Springer. 1939. RM 6,90.

Dieses handliche Büchlein, von dem zweieinhalb Jahre nach dem Erscheinen der ersten Auflage bereits die zweite vorliegt, behandelt die Untersuchungsmethoden für Stahl und Eisen, Metalle, feuerfeste Steine, Gas, Wasser und Kohle, wie sie in den Werken der Stahlindustrie gebräuchlich sind. Das Schwergewicht ist dabei auf diejenigen Verfahren gelegt, welche sich im Laboratorium der Firma Rheinmetall-Borsig A.-G. besonders bewährt haben.

Das Buch nimmt in seiner Anlage weitgehend Rücksicht auf die Bedürfnisse der Ausbildung von Lehrlingen und Volontären und dürfte in dieser Hinsicht bei geeigneter praktischer Anleitung auch seinen Zweck erfüllen. Es finden auch moderne potentiometrische Verfahren Berücksichtigung. Im Schlußkapitel werden die Bereitung und Titerstellung der Lösungen zur Maßanalyse, die Wiedergewinnung der Molybdänsäure aus den Filtraten der bei der Phosphorbestimmung anfallenden Niederschläge und ebenso die Wiedergewinnung von Silber aus silberhaltigen Chemikalien und Fixierbädern besprochen.

Der Mikroanalytiker kann aus dem Werkchen für manche mikroanalytische Untersuchungen ähnlicher Art sicherlich einige Anregungen entnehmen.

F. Hecht-Wien

Autorenverzeichnis.

Ballaban, H. E. 1,2-Diaminoanthrachinon-3-sulfosäure als Kupferreagens in der Tüpfelanalyse. S. 57.

Bayer, F. Gasanalyse. (Besprechung.) S. 140.

Beck, G. Zur Mikrochemie der seltenen Erden. S. 47.

Benedetti-Pichler, A. A., and *R. A. Paulson.* Quantitative microdeterminations with the use of ordinary analytical balances. S. 339.

Brennecke, Erna. Schwefelwasserstoff als Reagens in der quantitativen Analyse. (Besprechung.) S. 348.

Centre, le, de microchimie de Bruxelles. S. 243.

Chemische Analysen-Methoden (Schiedsanalysen) für Aluminium und Aluminium-Legierungen. (Besprechung.) S. 246.

Cimerman, Ch., et *P. Wenger.* Étude microanalytique du zinc au moyen de l'o-oxyquinoléine IV. Microséparations. S. 76.

Cimerman, Ch., s. *Wenger, P.* S. 85.

Corbaz, A., s. *Wenger, P.* S. 85.

Division of Microchemistry (American Chemical Society). (Sitzungsbericht.) S. 128.

Donau, J. Mikroelektrolytische Bestimmungen in kleinen Flüssigkeitsmengen. S. 14.

Donau, J. Beiträge zur Behandlung kleiner Niederschlagsmengen. S. 189.

Dunn, Rayburn, Kaoru Inouye, and *Paul L. Kirk.* The microscopy of the amino acids and their compounds IV. Picrolonates. S. 154.

Erdös, J., and *B. László.* Organic chemical operations with small amounts of material (Summary of previous publications). S. 211.

Fischer, R. Über den Nachweis von Ammoniak, Calcium und Strontium mit organischen Nitroverbindungen. S. 67.

Ghimicescu, Gh. Einige Mikromethoden zur Bieruntersuchung. (Sammelreferat.) S. 197.

Gmelins Handbuch der anorganischen Chemie. Systemnummer 27: Magnesium, Teil B, Lfg. 4; Systemnummer 35: Aluminium, Teil A, Lfg. 6; Systemnummer 59: Eisen, Teil F II, Lfg. 1; Systemnummer 68: Platin, Teil A, Lfg. 1, Teil B, Lfg. 1. (Besprechungen.) S. 247, 349, 350.

Grangaud, René. Nouvelle méthode de lavage et d'isolement du sulfate de baryum dans le microdosage du soufre par gravimétrie. S. 52.

Gstirner, F. Chemische Vitamin-Bestimmungsmethoden für das chemische, physiologische und klinische Laboratorium. (Besprechung.) S. 247.

Hynes, W. A., and *L. K. Yanowski.* Studies on the application of salts of complex cations to the microscopic detection of anions. IX. Monoaquopentamminocobaltic chloride (Roseocobaltic chloride). S. 335.

Hynes, W. A., s. *Yanowski, L. K.* S. 161.

Inouye, Kaoru, s. *Dunn, Rayburn*, S. 154.

Janke, A. und *E. Mikschik.* Über eine Mikromethode zur potentiometrischen Formoltitration. S. 176.

Jurány, H. Ein neuer empfindlicher Mikronachweis von Thallium. S. 8.

Jurány, H. Ein einfaches Filtergerät zum Filtrieren und Auswaschen von

Niederschlägen auf dem Objektträger. S. 185.
Karlik, Berta. Der Heliumgehalt von Steinsalz und Sylvin. (Sammelreferat.) S. 216.
Kirk, Paul L., s. *Dunn, Rayburn.* S. 154.
Klut, H. Untersuchung des Wassers an Ort und Stelle. (Besprechung.) S. 245.
Kocsis, E. A. Neue Daten zum Tüpfelnachweis einiger Ionen. S. 180.
Kroupa, Edith. Mikrogravimetrische Trennung von Zink und Uran, S. 1.
Kroupa, Edith. Geologische Zeitmessung durch Monazitanalyse. I. Bestimmung von Blei und Thorium. S. 165.
Kyllingstad, O. S., s. *Raeder, M. G.* S. 112.
László, B., s. *Erdös, J.* S. 211.
Lindahl, P. E. Ein Zusatzgerät zum Vermeiden des Übersaugens bei dem Mikro-Kjeldahlapparat von *Parnas-Wagner.* S. 195.
Lindpaintner, E. Mikroskopische Untersuchungen an polymorphen Substanzen. II. Mitteilung. S. 21.
Lübke, A. Das deutsche Rohstoffwunder. (Besprechung.) S. 245.
Manly, R. S. A list of micromethods for the determination of calcium and phosphate. S. 145.
Meyer, H. Analyse und Konstitutionsermittlung organischer Verbindungen. (Besprechung.) S. 140.
Microchemical Sub-Group, Philadelphia Section, of the American Chemical Society. (Sitzungsbericht.) S. 240.
Mikschik, E., s. *A. Janke*, S. 176.
Mitteilung der Schriftleitung. S. 248.
Nadler, Edith. Fortlaufende Literaturübersicht über Arbeiten mikrochemischen Inhaltes. S. 118, 231.
Niezoldi, O. Ausgewählte chemische Untersuchungsmethoden für die Stahl- und Eisenindustrie. (Besprechung.) S. 350.
Paulson, R. A., s. *Benedetti-Pichler, A. A.* S. 339.
Polaczek-Wittek, Annemarie, s. Schmid, Leopold, S. 42.
Raeder, M. G., und *O. S. Kyllingstad.* Über die quantitative Abscheidung kleiner Goldmengen aus Lösungen durch Mikroelektrolyse. S. 112.
Rây, Priyada Ranjan and *Tripura Charan Sarkar.* Quinaldinic acid as a micro-reagent IV. Estimation of zinc in the presence of copper, or of silver and mercury. S. 64.
Sarkar, Tripura Charan, s. Rây, Priyada Ranjan. S. 64.
Schmid, Leopold und *Annemarie Polaczek-Wittek.* Blütenfarbstoffe von *Potentilla tormentilla.* S. 42.
Spectrochimica Acta. (Besprechung.) S. 244.
Tschermak-Seysenegg, A. Mikro-Kristallisationsstudien an übersättigten Lösungen. S. 96.
Vorratspflege und Lebensmittelforschung. (Besprechung.) S. 141.
Weber, K. Inhibitorwirkungen. (Besprechung.) S. 142.
Weihrich, R. Die chemische Analyse in der Stahlindustrie. (Besprechung.) S. 143.
Wenger, P., Ch. Cimerman et *A. Corbaz.* Sur le micro-dosage du cobalt au moyen de l'acide anthranilique II. Technique de *Pregl.* Technique d'*Emich.* Influence les sels étrangers. S. 85.
Wenger, P., s. *Cimerman, Ch.* S. 76.
Whitmore, W. F., and *C. A. Wood.* Chemical microscopy of some toxicologically important alkaloids. S. 249.
Wood, C. A., s. *Whitmore, W. F.* S. 249.
Yanowski, L. K., and *W. A. Hynes.* Studies on the application of salts of complex cations to the microscopic detection of anions. VIII. 1,2-Chloroaquotetramminocobaltic chloride. S. 161.
Yanowski, L. K., s. *Hynes, W. A.* S. 335.

Herausgeber, Eigentümer und Verleger: Julius Springer, Wien I, Schottengasse 4. — Für den Inhalt verantwortlich: Dr. *Friedrich Hecht*, Wien IX, Währingerstraße 38. — Druck: Manzsche Buchdruckerei, Wien IX, Lustkandlgasse 52.